PRINCIPAL CONTENTS IN THIS ISSUE:

International Trade

SINCE the Government released some information on the trend of British exports during the war years there has been a growing interest in the subject of international trade by members of all parties in the House of Commons. Although no figures of exports are given in the Board of Trade returns, sufficient information is given to confirm the world pre-war view of the position recently given by President Roosevelt in his lease-lend report. They show that in 1943 British exports had fallen to 30% of their 1938 volume and to 49% of their 1938 value. To this it may be added that the trend has continued to decline in 1944, and in recent months the position appears to be deteriorating from bad to worse.

It is important that these facts should be properly appreciated, especially as, for some time past, members of Parliament seem to have been concerned primarily with demands for improved living standards than with the means for providing those improvements in Britain's social structure. That we live by faith seems to be taken too literally, with relatively little attention to the economic structure of the country. Higher wages for less hours of labour, family allowances, higher old age and disability pensions and unemployment benefits, housing and replanning programmes, and improved educational facilities are all very desirable, but the cost must be borne by trade and industry and more attention could profitably be devoted to this important aspect. Even the recent White Paper on the demobilisation plan for war workers gives little guidance on the restoration of normal trade.

It is true that war production has been and is to-day on a high level, although absenteeism is causing managements considerable trouble—a problem which should engage the attention of the Trades Union Council—but, while it is important to endeavour to satisfy demands for improved living standards, immediately after the war, the need is more urgent to seek the fullest employment of British economic resources. Looking ahead, there is no more pressing problem for trade and industry than that of laying plans to revive export trade, and, with proper safeguards, putting them into operation, without undue delay. Apart from production for the Forces, only one industry should have priority in materials and labour over those required to meet urgent overseas requirements, namely, housebuilding and its essentials.

To improve living standards necessitates purchases abroad, either of raw materials or of goods not available in this country and the purchases that a country can make are limited by the value of the goods and services that it can sell. International trade enables countries and localities to develop the industries best suited to them, and it helps to raise consumption by enabling consumers to take advantage of specialisation in economic activities. Britain, probably more than any other industrialised country, cannot afford to lose sight of the fundamental principles that international trade is an exchange of goods and services for goods and service. With this in view, it is discouraging, to say the least, that orders placed in this country from abroad have been handed over to the United States and apparently for subsequent orders from the same source to be sent direct to the United States for execution. This may be an odd instance, but, in principle, it increases the difficulties with which trade and industry in this country are confronted.

Apparently, in this country production for the Forces continues to absorb more materials than are available excepting through lend-lease channels and it occupies the services of all available labour in the industries concerned. Britain's steel production, although on a high level, evidently does not wholly satisfy war needs, thus no surplus is yet available which could be used in manufactures for overseas trade. On the other hand, in the United States, substantial percentages of raw materials produced are being used for home consumption and for export purposes. It is extremely unlikely that when the lend-lease agreement was made, the United States had any intention of obtaining a strangle-hold on Britain's export trade, it seems probable, therefore, that some concession could be made by permitting small percentages of available raw or semi-finished materials to be set apart for export purposes, without sacrifice to the Forces, or causing unfavourable comment in the United States.

There can be little doubt that during the immediate post-war period, and especially after the defeat of Germany, international trade will present numerous problems and some form of international agreement and machinery must be devised to control it, at least during the reconstruction period. Thus, export control must remain in operation for some time after the war, and, however diffident one may feel in deciding on the maintenance of such control, because of the difficulties of agreement, of finding common denominators and sequences of urgency, and the possibilities of delay and frustration, such a course is desirable. Many will regard it as a choice between two evils, but the evil of a "free for all" fight for goods and markets appears to be by far the worst. Export control would obviously be of a temporary character, and there are indications of this in the recent Government White Paper, but a lead is required to assist export planning on a long-term basis and to remove anomalies that exist.

Reinstatement in Civil Employment

RARELY in the history of this country have so many social reforms been contemplated in so short a time. Education, full employment and social security plans have been announced by the Government in their logical order, and gradually the framework within which the economic life of the nation is to be built takes shape. The effectiveness of all these plans, however, will depend to a large degree upon the success with which the full employment policy is executed, but there are many obstacles to be overcome before a high and stable level of employment after the war can be achieved.

There will be an awkward transition period, when industrial activity will be diverted from war to peace production. This change-over will begin with the defeat of Germany, and it will be necessary to find jobs for those workers displaced by the diminution in war production. Although there will be dislocation in the initial stages, it is necessary when making plans for the equitable allocation of labour to work available the claims of demobilised men must not be overlooked. It is of primary importance to establish in the minds of these demobilised men the fact that they are being dealt with fairly. In this connection, considerable interest is attached to the reinstatement plan of the United Steel Companies, Ltd., of Sheffield, which are the largest steel producers in the British Commonwealth.

For some considerable time the United Steel Companies have been giving careful thought to this important question. It is felt that with the great majority of their employees now serving in H.M. Forces, the paramount desire will be to get back to their old job as quickly and comfortably as possible. It is true, of course, that reinstatement is required by Law, but the company feels that something more should be done to make the transition from Service to civil life as smooth as possible. Authoritative committees have therefore been appointed at each branch, whose task will be not only to welcome those returning from the Services, but to help them to deal with the problems of adjustment, which are bound frequently to arise, and to ensure that they suffer no disadvantage through their prolonged absence from civil employment.

In addition, it is felt that there will be a number of men, particularly those who left as juniors or apprentices, who have evinced outstanding qualities of ability and leadership in the Services, and who should be given the opportunity of developing those qualities in civil life, both to their own benefit and that of the community. A special training scheme has, therefore, been evolved to enable such men to qualify for important positions on the executive and administrative staff as and when vacancies occur.

The course of training is planned to last for twelve months and to provide the necessary incentive to candidates to prove their ability. A salary will be arranged individually for each candidate, taking into account age, previous experience, and the pay of the rank attained in the Services.

Such a scheme can only interest a minority, but it is felt that no plan for the satisfactory reinstatement of ex-Servicemen would be complete if some machinery were not devised to develop the qualities of ability and leadership which have been disclosed in military service.

Obviously, it should be the duty of industry to make its employees, released for service in the Forces, realise that every effort is being made to ensure their positions on return to civilian life. Reinstatement affects by far the majority of men in the Forces, and until satisfactory arrangements are made for their absorption by industry all the social security proposals will be valueless, since an essential requirement of men in the Forces is the assurance of work on demobilisation. The scheme designed by the United Steel Companies goes further than this in enabling men with special aptitudes to qualify for important positions on the executive and administrative staff. The directorate of the company is to be congratulated for its contribution to an important aspect of demobilisation.

The Iron and Steel Institute
Annual General Meeting

The Annual General Meeting of the above Institute will be held at The Institute of Civil Engineers, Great George Street, London. S.W.1, on November 23 and 24. The meeting will be devoted to a discussion on blast-furnace operations and problems based on the following papers :—

Paper No. 1 : " Ironmaking at the Appleby-Frodingham Works of the United Steel Companies, Ltd." By G. D. Elliott and the Staffs of the Appleby-Frodingham Ironworks, Scunthorpe, and of the Central Research Department, Stockbridge (The United Steel Companies, Ltd.).

Paper No. 2 : "Considerations on Blast-Furnace Practice." By T. P. Colclough, D.Sc., M.Met., F.R.I.C. (London).

PROGRAMME.

Nov. 23.   Morning Session : 11—11-10 a.m., Transaction of official business.
11-10—11-30 a.m., Presentation of Papers Nos. 1 and 2.
11-30 a.m.—12-45 p.m., Discussion on Fuel Consumption, based on :—
Paper No. 2.—Relevant sections.
Paper No. 1.—Section IV, Blast-Furnace Coke.
Section IX, The Utilisation of Fuel in the Blast-Furnace.

Nov. 23.   Afternoon Session : 2-45—5 p.m., Discussion on Furnace Operation and Problems, based on :—
Paper No. 1.—Section III, Furnace Plant Design and Lay-out.
Section VII, Furnace Operation and Operating Problems.
Section VIII, Scaffolds.
Section X, Hearth Breakouts.

Nov. 24.   Morning Session : 10-30—11-45 a.m., Discussion on the Preparation of the Burden (with special reference to Ore Beneficiation and Sinter), based on :—
Paper No. 2.—Relevant sections.
Paper No. 1.—Section II, The Blast-Furnace Burden.
11-45 a.m.—1 p.m., Discussion on Refractories, based on :—
Paper No. 1.—Section V, Blast-Furnace Refractories.
Section VI, Hot-Blast Stove Refractories.

Arc Welded Cutting Alloys

By E. C. Rollason, Ph.D., M.Sc., and P. Harris, B.Sc.

Alloys of high hardness have many applications when deposited on tougher materials ; they are applied where high hardness, high polish and low co-efficient of friction and high abrasive resistance are required. For this article, attention is especially directed to their application for cutting purposes and to their deposition by the arc welding method.

Fig. 1.—Isothermal tempering curves of as-deposited weld metal.

INCREASING attention is being directed to the use of metallic arc welding as a means of facing engineering parts with hard metal and for the building up of cutting edges. At the outset, however, it is important to divide cutting processes into two classes :—

(1) Cutting where the tool edge is subjected to heat likely to produce softening and subsequent failure, for example, lathe tools and milling cutters.

(2) Cutting without appreciable rise in temperature of the cutting edge—for example, cold shearing blades and clipping dies. For such a purpose a hard surfacing electrode producing a weld containing moderate quantities of elements, such as chromium and molybdenum, is satisfactory. Hardnesses of 650 V.P.N. (Vickers' Pyramid Number) can be reached in the as-deposited condition.

The main object of this article, however, is to deal with more thermostable alloys falling in the first class.

It is convenient when considering the requirements of a hard alloy merely from the cutting point of view to regard the various ways by which a tool may fail. These may be listed :—

(1) Abrasion.
(2) Spalling and crumbling of the cutting edge.
(3) Loss of hardness by tempering.

Abrasion failures occur either by wear and tempering on the top face of the tool as the chips slide over it, or by wear on the front face immediately below the cutting edge. The hollows formed gradually enlarge until they spread to the cutting edge, causing its collapse. A primary requirement of a cutting deposit is, therefore, the incorporation of elements giving high abrasion resistance.

Crumbling failures are due to an inherent brittleness of the cutting material, and are accentuated by chatter which is due to the repeated building up and breaking down of the adhering deposit of work material to the cutting edge.

The third factor brings out the important fact that mere high hardness is not a criterion of cutting suitability in an alloy—the alloy must be hard, but able to retain a large measure of this hardness at elevated temperatures since the heat generated at the cutting edge raises its temperature considerably, especially if the thermal conductivity of the material is poor. Most tool materials contain dispersed carbides which are largely unaffected by heat, but in addition martensite is usually present, a phase which is susceptible to softening by heat. Thus, in ordinary plain carbon tool steels the martensite commences to soften at 200° C., precluding its use for high-speed cutting, whereas high-speed steel, in which the martensite is stabilised at high temperatures by

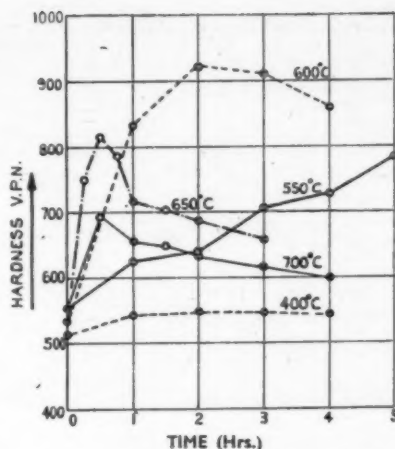Fig. 2.—As-deposited with rapid cooling. Austenite matrix network of coarse carbide and massive carbide with surrounding fringe of an austenite decomposition product. × 2000.
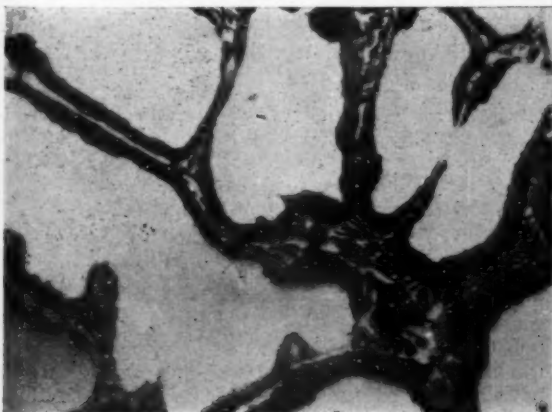
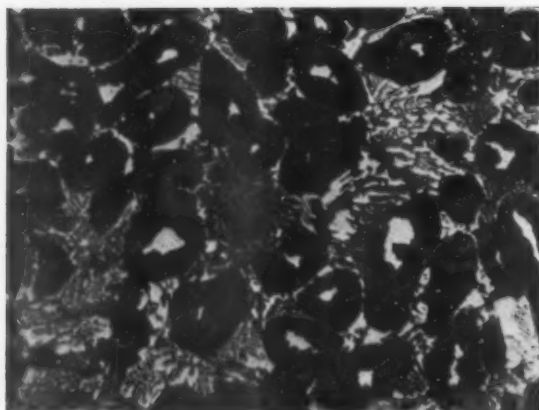Fig. 3.—As Fig. 2 in tempered condition. Decomposition of austenite to a thermostable martensite. × 2000.

Fig. 4.—As deposited with slow cooling. Coarse carbide eutectic and massive carbides with austenite grains practically totally reacted. × 500.

alloying agents, retains its hot hardness up to red heat.

The above factors briefly outlined can be achieved in more or less measure in deposits formed by arc welding. There are three main types of electrode whose deposits may be used for cutting purposes :—

    (1) Stellite alloys.
    (2) High-speed steel deposits.
    (3) Special alloys.

Stellite alloys have found limited use as cutting deposits. These alloys are more useful for hard-surfacing purposes, especially where corrosion resistance in addition to abrasion resistance is required.

High-speed steel core wire electrodes are available which yield deposits comparable roughly with an as-cast high-speed steel, though much tougher, and which are immediately ready to be ground for use. They have a high initial hardness, about 700–720 V.P.N., and the substitute molybdenum steels—e.g., molybdenum 8, chromium 4, vanadium 1½, tungsten 3—seem to be more easily deposited and freer from porosity than the standard high tungsten types. There is no actual need for heat-treatment after deposition, but some secondary hardness can be developed at about 600° C. If it is desired to machine the deposit, it can be fully softened by annealing at 800° C., followed by the usual hardening heat-treatment subsequent to the machining operations, and in view of the fact that the substitute molybdenum steels decarburise so easily, precautions should be taken against this.

A New Arc Deposited Cutting Alloy

With regard to special alloys, which cannot be classed strictly as stellite alloys or high-speed steels, it may be mentioned that the deposit is achieved synthetically by employing a mild steel core wire electrode with a heavy metallic coating containing the alloying elements. By this means great versatility of properties far in excess of ordinary high-speed steel deposits can be achieved, and care can be taken that the fundamental requirements of hot hardness and abrasion resistance are fulfilled. Correct choice of coating components and provision for effective deoxidation in view of the large amount of carbon carried results in soundness, and the boiling and

decarburisation which is a feature of high-speed steel electrodes deposited too hot is absent.

A typical example of a recent alloy in this field is exemplified in the response of the deposit to heat-treatment, as shown in Fig. 1. As a result of heat-treatment at various temperatures, the curves are characteristic of the separation of a hard, but not fully thermostable phase, and all hardnesses ranging from about 480–900 V.P.N. can be achieved with degrees of control which will be evident from the nature of the isothermal curves. For most common purposes a temperature of 600° C. is suitable for obtaining a reasonable amount of control commensurate with a rapid hardness increase.

In order to explain the practical application of this alloy it is necessary to consider the metallurgical features. Ordinary rates of cooling after arc depositing result in a structure illustrated in Fig. 2. This shows a carbide network, which is partly eutectic and partly massive, surrounding a highly supersaturated austenite containing molybdenum, tungsten and carbon in solid solution. It will be noted that a small fringe of an intermediate bainitic product surrounds the carbide ; it was nucleated at this face, growing into the austenite.

This structure results after depositing the material in the form of beads on a cold base and allowing ordinary slow air cooling. If this alloy is then heat-treated, for example, 1 hour at 600° C., the austenite decomposes to a highly alloyed thermostable martensite (Fig. 3), resulting in a material which has good cutting properties for general turning and shaping work, where conditions are not too severe. The drawback is due to a certain amount of brittleness, which is caused by the massive carbide in the eutectic network. In actual practice the duplex process of depositing and subsequent tempering can be avoided by depositing a fairly large mass of the material on a preheated base—about 300° C. is adequate, the final material containing precipitated martensite, due to the tempering effect of successive beads and final slow cooling. Fig. 4 shows the kind of structure produced with such a technique. There is much massive carbide and transformation product, with a little martensite. If, of course, only a small mass is deposited in a large cold base, the cooling rate will be high and no martensite will be found, necessitating its later development by heat-treatment.

Such tools should be considered from the cutting-tool point of view as intermediate between high-speed steel and sintered carbide tools. Thus a fairly large lip angle should be allowed on turning tools, to give good support to the tool edge and the tool should be supported rigidly to avoid chattering (minimum overhang). There must be adequate support for the deposited tip by the mild steel base ; there should be at least twice the thickness of mild steel below the tip as the tip is thick itself, in fact the smaller the amount of metal deposited and the larger the amount of mild steel below to give a cushioning effect the better, provided an adequate hardness is obtained as a result of self-tempering.

The formation of the undesirable massive carbide in the eutectic network can be suppressed if slow cooling below 1,200° C. is avoided. This can be achieved by puddling the alloy in a graphite refractory mould on to a preheated mild-steel base, followed by oil or air-blast quenching from 1,200° C.—i.e., as soon as welding has terminated. This results in a well-formed eutectic network free from massive carbide (Fig. 5), with residual
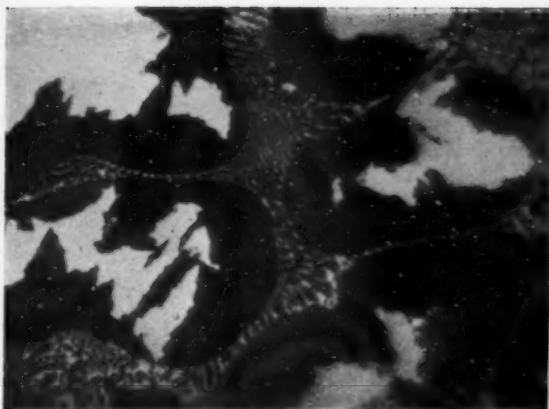
Fig. 5.—Puddled and oil quenched from 1200° C. Fine well formed eutectic network. Some transformation product growing into austenite grains. × 1200.

Fig. 6. As Fig. 5, but tempered 1 hour 600° C. Shows remainder of austenite decomposed to martensite. Note fine eutectic and absence of massive carbides.

austenite and some transformation product (arborescent bainite). On tempering this alloy, the austenite transforms to martensite, the number of plates increasing with time and temperature, resulting in a structure as shown in Fig. 6. This structure has super cutting properties—at least twice as effective as 18–4–1 high-speed steel as measured by breakdown tests as the Table I shows. Fig. 7 illustrates the method using a mould round the steel shank.

TABLE I.
BREAKDOWN TESTS.
Cutting 90 ton per sq. in. 3% chrome-molybdenum steel.

Tool.	Treatment.	Speed, Ft. per Min.	Cut.
Hardex	Oil quenched from 1,200° C. Tempered 580° C. ½ hour ..	77 104	½ in. 0·004
18–4–1 High-speed Steel	Normal	30	½ in.

Thus there are two techniques of deposition for this material arising out of its physical behaviour. In the first instance, bead running on a preheated base to achieve some measure of self-tempering, this method being quick and convenient and giving a material whose properties are adequate for general cutting purposes, but having some slight limitations of brittleness. On the other hand, by slightly complicating the method of preparation, a material of vastly superior properties is obtained, and if difficult cutting conditions are liable to be encountered the extra trouble is well repaid.

The above, then, are typical examples of the types of deposit which may be formed by arc welding and which have cutting properties. The advantages and uses of making such deposits have in the main an economic basis, in that the saving by hard-tipping the edges of a mild-steel body in preference to forming the whole from high-speed steel and heat-treating, is very considerable, especially to-day, when the need for conserving tungsten and similar metals is so great. Furthermore, it is possible to salvage damaged high-speed-steel milling cutters, etc., by arc welding, provided the correct technique is used.

The tipping of mild-steel tool shanks or milling cutter blanks with either high-speed steel or special alloy electrodes is straightforward. The work should be preheated to about 250° C. in the case of the special alloy mentioned, as this ensures a slow rate of cooling and allows of the development of about 700 Vickers hardness degrees on cooling. This degree of hardness is associated with a sufficient toughness to withstand the shocks involved in planing and turning operations, provided the precautions noted previously with regard to tool design are observed. Even so, it should be emphasised that this material cannot compete with sintered alloys for cutting properties.

If very small deposits are made, it is necessary to harden afterwards by heat-treatment, as owing to the low heat input the rate of cooling will be rapid and the initial hardness low. Note, that if great stresses are put on the base metal a 3% nickel constructional steel should be used in preference to mild steel. Apart from

Fig. 7.—Illustrating method and stages in procedure in producing a puddled tool.

the saving resulting from the use of mild-steel blanks, there is a saving if the cutter suffers subsequent damage. Thus, if a high-speed-steel cutter is jammed, a tooth may break off and a crack may spread into the body of the cutter owing to the inherent lack of ductility of the material, thereby rendering it a total loss. With a mild-steel body of high ductility, the damage would be confined to breaking off the welded tooth—a defect which

Fig. 8.—Result of depositing tool tipping alloy on an unpreheated radial milling cutter (8 in. dia. × ½ in.). Note origin of crack at re-entrant angle of tooth.

can be easily remedied. The resilience of a mild-steel shank absorbs a large measure of the shocks encountered at the tool tip and prevents their transmission to the machine thereby.
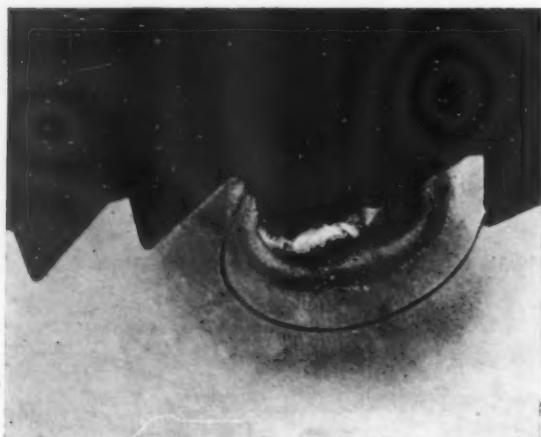
Employing high-speed-steel electrodes, the technique is bead application similar to the above; a preheat of 300°–400° C. is useful, as the delayed cooling develops some secondary hardness.

It is impossible to tip-up thin cutting edges directly, as the heat of the arc immediately destroys these, so that it is desirable to grind them flat or to grind a step at the top of a tooth to receive the hard deposit. Usually 3–4 superimposed beads are sufficient to build up the required height and to escape the diluting effect of the base metal.

Salvage of High-Speed-Steel Tools

The repair and salvage of high-speed-steel tools in the hardened condition is a very difficult matter. The steel is in such an inelastic condition that the heat input from the arc if at all excessive sets up stresses which are unable to be relieved except by cracking. A preheat of 500° C. while in some measure reducing the cracking tendency, does not eliminate it, and no welding involving a large heat input can be regarded as safe under these conditions.

Fig. 8 shows a portion of a milling cutter on which an attempt to build up a broken tooth has produced cracking from the root of an adjacent tooth owing to the high concentration of stress. The rounding off of these sharp corners by the deposition of small beads of mild steel helps to minimise the high stress concentration, but frequently does not entirely eliminate the trouble.

In all the above cases the input of heat has been fairly large—e.g., a 12-gauge electrode with the arc operating for some 20 secs.—but it has been found possible to deposit on high-speed steel without cracking if the heat input is minimised by using a small gauge electrode (16-gauge) and allowing the arc to be maintained for 2 to 3 secs. at the most.

Fig. 9B shows a high-speed steel broach tipped in this manner. Fig. 9A shows the same specimen tipped without any attempt to minimise heat input. The limitations of this method are immediately apparent in that only very small masses of metal can be deposited, whereas in practice tools may suffer heavy damage, necessitating large deposits.
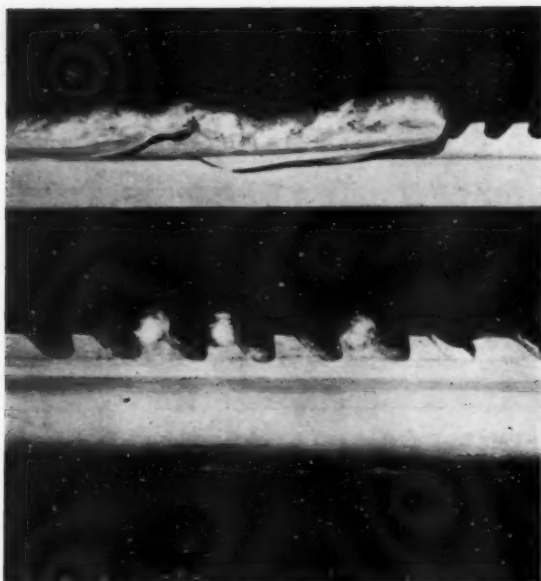
Figs. 9a and 9b.—Incorrect and correct procedure as applied to a high-speed steel broach. Upper specimen—no pre-heat and massive deposit; lower specimen—400° C. preheat and application of minimum amount of deposit.

In such cases, therefore, it is advisable fully to soften the high-speed steel by annealing at 800° C., welding at about 500° C., and allowing the specimen to cool slowly in lime or ashes to avoid thermal shock. If the specimen is small or of thin section, it may be necessary to maintain its preheat during the welding. This method, of course, requires that all the cutting edges must now be tipped-up, as the material is in the fully softened condition, and electrodes of the high-speed steel and special alloy types are available, which can be deposited on high-speed steel without porosity and cracking.

Although the emphasis above has mainly centred on cutting requirements, the other uses of the material are too numerous to deal with fully, but any applications where high hardness, high polish and low coefficient of friction and high abrasion resistance are required can be fulfilled with all the versatility which arc deposition confers.

Acknowledgment is made to Murex Welding Processes, Ltd., for much of the data contained in this article.

The "Foseco" Calculator

THE need of a reliable guide for pouring temperatures for copper and nickel alloys has often been expressed; until recently, however, no suitable guide has been available. The importance of reasonable accuracy in the pouring temperature of these alloys has long been realised, and in response to requests the "Foseco" calculator has been produced which supplies pouring temperatures for most of the copper and nickel alloys. The manipulation of the calculator is very simple. We have no doubt that this calculator will be very useful in non-ferrous foundries. It is supplied, together with detailed directions, by Foundry Services, Ltd., Long Acre, Nechells, Birmingham, 7; price 7s. 6d. post free in the United Kingdom.

Some General Aspects of Continuous Casting

By V. Kondic, B.Sc., Ph.D.

Continuous casting has been known and practised for a century or more, but it is only during recent years that rapid progress has been made in its development. To-day, commercial technique has been developed to permit one of many processes to be applied to a wide range of ferrous and non-ferrous metals and it is probable that further advances in technique will soon be made. Some general aspects are given in the application of continuous casting in the production of ingots or billets.

THE overwhelming majority of wrought metallic products originate from solid castings known as ingots or billets which are subsequently forged, rolled, extruded, or by some other operation transformed into finished or semi-finished articles. It has been estimated that about 70 to 75% of the entire production of aluminium alloys is cast into billet form, and there is no doubt that a similar situation prevails in the case of many of the other metals, both ferrous and non-ferrous. The selection of conditions governing the casting of billets depends on two main considerations :—

(a) The exclusion of structural defects which might give rise to failure during subsequent working operations— or impair the mechancal properties of the finished product,

(b) The casting should be carried out on an economical basis from the foundry production point of view.

The familiar and well-established process of casting billets individually and discontinuously has for some years past been seriously challenged, especially in the field of non-ferrous alloys, by the process known as continuous casting. It would perhaps be of some interest to producers considering a change-over to this latter process to compare the two methods of casting billets, bearing the above-mentioned points in mind.

General Aspects

The general considerations involved in the casting of billets into cast iron, copper-faced, water-cooled, or other similar moulds by the usual methods are too well-known to warrant a further review of the subject. The main features of continuous casting are, however, less familiar to non-users of the process. Descriptions of various types of continuous casting machines are already available in the technical literature*. It is not the purpose of this article to compare the engineering merits and demerits of existing casting machines, because there is no doubt that from the engineering point of view further refinements will be introduced as the process develops further. Continuous casting is, however, not only an engineering but also a new metallurgical development, involving a new method of cooling cast billets. From this point of view it may be noted that two main methods have so far been used commercially : (1) the continuous mould principle (Soro process), and (2) the short mould principle (Junghans, Alcoa, Williams and similar processes).

Judging from the information available, it appears that the second method is progressing far more rapidly than the first, and can be utilised in a variety of ways for many different metals and alloys. This article discusses the salient features of this second method of cooling.

The chief considerations which have to be taken into account when starting a new continuous casting unit may be summed up as follows :—

(a) The necessity for preliminary development work.

(b) The choice of the type of machine.

(c) The initial capital investment in building the machine.

(d) The advantages of the process from the economic point of view.

There is no single universal continuous casting machine which can be used without any modification to cast every metal or alloy ; most of the machines which have so far been made have been designed to meet the requirements of a particular alloy and billet size, or of existing foundry facilities. A prospective newcomer into the field of continuous casting may follow one of two courses :—

1. He may purchase the patent rights of machines which have already proved successful.

2. He may design independently a machine to suit his own particular requirements.

In this case some preliminary development work is necessary.

In view of the simplicity of the continuous casting process, and of the laws governing the solidification of metals, it is very doubtful whether the purchase abroad of existing patent rights ever proves the more satisfactory policy. The mechanical problems involved in the independent design of a machine are very simple and the amount of development work required on this side is small. A certain amount of preliminary work must, however, be carried out to determine the correct design of the mould, and the method of application of the cooling medium to the mould and the billet. For this purpose a small pilot machine is all that is necessary, and such a machine can be built at small cost.

Construction of Continuous Casting Machines

A continuous casting unit usually incorporates the following component parts, although each particular design introduces its own modifications :—

(a) Melting and pouring parts, i.e., furnaces, ladles, launders and distributors.

(b) Cooling parts, i.e., moulds, sprays, pumps, and the cooling medium.

(c) Moving mechanism, i.e., motors, hydraulic cylinders or rolls, which lower the billet during casting.

(d) Auxiliary parts, such as flow-meters, speedometers, etc.

It will immediately be apparent that the design of a continuous casting machine is an engineering as well as

a metallurgical problem. Failure to appreciate this fact is perhaps the reason why a large number of machines have been very costly failures.

While it is true that most of the machines at present in use differ in regard to the particular designs of these various components which they employ and in the way in which they are grouped together, yet it is equally true that all machines which have so far proved commercially successful involve the same essential feature, namely the cooling of the billet partly in and partly below the mould. In other words, different continuous casting machines have different engineering features, but the essential underlying metallurgical principle of of the method of cooling is the same.

The main purpose of the development plant is to determine for a given alloy the relationship between the speed of casting, pouring temperature and amount of cooling medium for a particular size and design of mould and method of cooling. From the data so obtained, optimum casting speed for a billet having given structural properties can be determined.

Melting and Pouring Parts.—A problem in continuous casting should always be considered in relation to the parallel problem of the melting of the metal. If the existing facilities of the foundry permit, direct transfer of the molten metal from the furnace to the casting machine is certainly preferable to the use of a ladle as an intermediate carrier. The saving in labour and time are obvious advantages of the direct method, and it should also be borne in mind that it involves smaller oxidation and skimming losses and also allows much easier control of the temperature of the metal during casting. The furnace may be tapped either by tilting, by bottom pouring, or through a suction pipe ; the choice depends mainly on the size of the furnace, the size of the billets being cast, and the number of billets being poured simultaneously. Simplicity of design and ease of maintenance are greatly in favour of the method of tilting and using a launder and distributors to obtain a number of streams when necessary. With a very large melting furnace and small billet sizes the use of ladles is unavoidable.

Cooling Parts.—The design of the mould for casting a particular alloy, and the choice of the method of cooling the mould and billet can only be determined experimentally. A very simple, and so far most successful, type of mould is a shell having thin walls of the desired section and open at both ends. A variety of materials, both metallic and non-metallic can be used for making moulds, the choice depending on the heat conductivity required. Carborundum, graphite, copper, aluminium and iron-base alloys have all been used.

Some non-ferrous alloys such as brasses, tin and phosphor bronze, silicon-aluminium alloys and certain others can be cast readily into copper or aluminium alloy moulds. The chief requirement of the mould in this case is sufficient hardness to give good wear. It is only with those alloys such as the iron base alloys which are more difficult to cast due to the very high total heat to be abstracted, and those ferrous and non-ferrous alloys being hot short, or having high contraction in the solid state leading to the development of internal stresses and cracking of the billets, that more careful consideration of the choice of the mould material and design of the mould is necessary. In such cases the thermal conductivity of the mould material is a more important factor, as is also the correct cooling of the billet and the arrangement of the sprays. In the case of the readily castable alloys, however, cooling is carried out in a manner determined largely by consideration of the maximum possible casting speed. Heat may be abstracted from the metal in two ways, laterally, through the mould walls, and longitudinally by quenching below the mould ; the cooling arrangements may be so adjusted that either of these processes becomes dominant, but in general a combination of both is used.

Experience so far obtained with the various types of machines goes to show that the design of the mould, the way in which it is cooled, and the method of introducing the liquid metal are of equal importance to the choice of mould material. Some physical aspects of the cooling of the mould have been discussed in an earlier article (see reference). The design of the mould varies according to whether longitudinal or lateral heat abstraction is required. The latter condition can not be achieved merely by using a mould material of high thermal conductivity ; it is necessary also to use finned mould surfaces, tapered moulds, and very fast rates of spraying. Composite moulds, oscillating moulds, and the introduction of the spray into the air gap between the mould and the billet are further refinements in the method of cooling. The liquid metal should be introduced into the mould in such a manner as to avoid carrying over any dross, to minimise turbulence effects, and to avoid un-uniform temperature gradients. Various designs of baffles, sometimes partly submerged in the liquid metal, are used for this purpose.

For cooling the mould and quenching the billet a variety of cooling media can be used, water, oil, and water and oil mixtures being the most common. In order to obtain a rapid rate of heat exchange the liquid is continuously circulated under pressure by pumps.

An alternative to the complete cooling of the billet to room temperature is to roll it while it is still hot ; this can be carried out by means of a set of rolls situated under the mould.

Moving Mechanism.—Several methods can be used for the continuous withdrawal of the billet from the mould. A hydraulic cylinder with a stroke equal to the length of the billet to be cast and having a range of controlled piston speeds has been favoured by many designers. A similar motion can also be obtained by means of a variable speed motor operating through a system of gears, clutches and counterweights. A very simple method is to use a pair of rolls below the mould. A big advantage of this system is that a flying saw or some other arrangement for the cutting of the billets at a constant length can be incorporated in the design so that the process of pouring is truly continuous as long as liquid metal is available. This is in contrast to the other processes of withdrawal in which pouring has to be stopped after a billet of a certain length has been cast, the billet removed and the pouring recommenced. At the commencement of casting the mould is closed by a block of metal which grips the billet in one of a variety of ways (dovetail key, wire extractors, screw system, etc.).

If the furnace is at the floor level then a casting pit is necessary. A simple solution seems to be to have the furnace or ladle raised and the billets removed at the floor level. Horizontal machines, as well as machines inclined at an angle have been made but, so far as is known, not with the same success as the vertical casting machines.

The chief auxiliary parts of the machine are flow-meters, speedometers, pyrometers, and length indicators. The function of such auxiliary instruments is not only to help in keeping a certain casting procedure constant, but also to serve as the tools for the investigation of the casting process.

Choice of the Machine.—A successful continuous casting machine should satisfy the following conditions :—

(a) A simple transfer of molten metal from the furnace to the machine.

(b) An efficient and easily controlled cooling unit.

(c) A reliable method of removing the billet.

(d) An easy method for the disposal of the cast billet.

(e) A simple method whereby the machine can be adapted to enable it to deal with various sizes and numbers of billets ; for this purpose the component parts should be readily demountable.

Few of the machines which have so far been described in the literature and which are at present in use in industry fulfil all these conditions, but progress is being made at the present time, and machines are now in use which have not yet been fully described.

The most important question, however, is : What economic and metallurgical advantages are to be gained by substituting a continuous casting process for ordinary methods of billet casting ? The answer to this question depends mainly on the kind of alloy and the size and type of billet which is to be cast. Common brasses, some of the bronzes, nickel, magnesium and aluminium alloys can be cast in a variety of shapes and sizes at speeds equal to or greater than those of ordinary casting methods in terms of tons per hour output. Harder and more complex alloys are still cast at rather slower speeds ; the reason for the use of the continuous casting process for such alloys lies in the fact that it yields sounder billets possessing a finer grain size and free from heavy segregations ; such billets have superior working properties and involve smaller scrap losses. In some extreme cases where certain severe working operations have to be carried out, only billets cast by the continuous casting process give satisfactory structural characteristics.

The initial capital investment required for building a continuous casting machine incorporating most of the parts described above is rather high. It should, however, be strongly emphasised that while the building of large machines is costly, the principles of continuous casting can readily be applied to smaller machines designed for casting billets of various sections and short length in a variety of alloys ; such machines are much cheaper and easier to construct.

Advantages of the Continuous Casting Process

While the characteristics of the continuous casting process depend, of course, on the particular design of the machine under consideration, the process as a whole may be said to possess the following advantages over the usual methods of billet casting ;—

(a) The billets produced are of higher quality, and so yield superior finished products with less scrap loss. Certain alloys which could not otherwise be worked may be cast in workable structural condition.

(b) In the case of some alloys the continuous casting process is more economical.

(c) A saving in the space required for both apparatus and storage is obtained, and further advantages result from improved cleanliness and reduced foundry maintenance costs.

(d) The same machine can be used to cast a variety of sizes and shapes of billets by changing the cooling parts only ; tubes and clad billets may readily be cast.

The chief disadvantages of the process are the high initial cost of the machines, and, in some cases, the expense incurred in initial development work.

So far as is known, the continuous casting process has been used chiefly for the casting of non-ferrous alloys. Recently, however, ferrous alloys have been also cast by this process. There is no doubt that further advances in both fields will soon be announced.

Forty Years' Technical Progress in the Gas Industry

IN his recent presidential address to the Institute of Fuel, Dr. E. W. Smith expressed himself as having no doubts about the future of the gas industry. Contrary to statements made in some quarters that for many years there has been little or no technical development in coal carbonisation, Dr. Smith stated that not only is gas being used more and more as a heating medium, but the possibilities in the future for the development of the carbonising industries are greater than they have ever been.

Advances are due to the united effort of all engaged in the gas industry—those who make and distribute the gas, those who design, build and manufacture plant in which gas is made or used, and the research men either in individual firms or undertakings or working under a scheme of co-operative research. The period of 40 years covered by the address was a time of flux, for new and revolutionary systems of gas manufacture were in process of development and new outlets for gas were available which demanded greater technical resources than were then available.

Laboratory investigations have enabled the behaviour of the coals in the retort to be forecast. Experience has shown that careful laboratory control of refractory materials and jointing cements used in construction is essential. Cast iron also plays a most important part in the carbonising industries, and the work of the British Cast Iron Research Association in improving the mechanical and physical properties of cast iron have been invaluable.

In coke production, in benzole recovery, in removal of naphthalene and water vapour from the gas, and in the use of coke-oven gas, the gas industry has done a great deal of useful work within the period under review. Dr. Smith deliberately refrained from elaborating on the research work in progress, but his closing words are especially noteworthy : " . . . The future of the industry depends first on the extent to which its technical men maintain its technical position, and, secondly, on the way in which the industry as a whole, as distinct from undertakings in themselves, is administered. Great things are expected from the committee of inquiry set up by the Ministry of Fuel and Power, but, whatever recommendations may be made, it will still rest with the rank and file of the industry to make the major contribution to its continued success."

Volumetric Determination of Copper in Aluminium Alloys

By G. Stanley Smith, B.Sc., A.R.I.C.

ROUGHLY speaking, there are two main types of methods used for the determination of copper in alloys of the duralumin type, the electrolytic and the iodimetric. The former may be considered as a referee method, yet it is used in many laboratories for routine analyses of large numbers of samples per day. The latter, which makes use of the reaction,

$$2CuSO_4 + 4HI = 2H_2SO_4 + 2CuI + I_2,$$
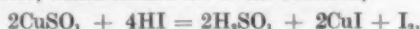
and subsequent titration of the liberated iodine with thiosulphate, is also widely used for works control purposes. It has been found, however, by many chemists that the method is apt to yield at times gross errors unless careful separation, which, of course lengthen the process, are carried out.

With a view to cutting out all unnecessary labour and to establishing an accurate titrimetric method an investigation was undertaken by the author a year or two ago of the errors that are likely to arise and of the best ways of avoiding them. As a result the simple method described below was worked out. Since that time it has been used in hundreds of analyses. It is very nearly fool proof and is equivalent in accuracy to the electrolytic method.

The volumetric method, as carried out in certain laboratories may give incorrect results because of (a) the presence of nitrous acid, (b) the presence of readily ionisable ferric and manganese salts, (c) loss of copper through absorption on ferric hydroxide when iron is separated by means of ammonia, or (d) incorrect acidity. In the method described below (a) urea is added to remove nitrous acid, (b) ferric and manganese salts are prevented from interfering by the introduction of a soluble fluoride[1, 2, 3, 4], giving complexes which do not react with potassium iodide, (c) there is no separation of iron from copper by filtration, and (d) the acidity is standardised.

Method

Reagents.—Sodium hydroxide, 20% solution; nitric acid, sp. gr. 1·2; urea, solid; ammonia solution, 1 vol. ammonia, sp. gr. 0·880, diluted with 4 vol. water; zinc acetate solution, prepared by dissolving 80 g. Zn. in 150 ml. glac. acetic acid and diluting to 800 ml. with water; sodium fluoride solution, prepared by dissolving 40 g. of sodium fluoride together with 12 ml. 20% NaOH in water and diluting to 1 litre. To be filtered as necessary; potassium iodide, potassium thiocyanate, solid reagents; starch solution; sodium thiosulphate, 0·05N standardised by any method which gives the theoretical factor.

Procedure.—Dissolve 2 g. of the alloy in 30 ml. of 20% NaOH. Leave on a boiling water bath for 15–20 mins., dilute to about 60 ml. with hot water, filter through a pulp pad in a funnel and wash with hot water. Then place the original beaker under the funnel, cover the funnel with a clock-glass and run in under the cover 5 ml. of HNO₃ (sp. gr. 1·2). Wash down the cover and when the liquid has passed through replace the beaker

by a conical flask and pour the solution in the beaker into the funnel, making sure that all the copper goes into solution. Wash beaker and filter with hot water. Bring the solution in the conical flask to the boil, add about 0·5 g. of urea and continue boiling for 5 mins. Then add dilute ammonia (1·4) carefully until the liquid changes in colour from yellow to green. Bring again to the boil, causing a further change in colour to clear brown. Add 20 ml. of zinc acetate solution, taking care that the solution does not froth over, and place the flask in running water to cool. Add 10 ml. of filtered sodium fluoride solution, followed by about 2 g. KI, and titrate with 0·05 N thiosulphate, adding starch and 2 g. KCNS towards the end of the titration. The end point is indicated by a colour-change from blue to brown.

No. of ml. 0·05 N thiosulphate × 0·159 = % Cu (on 2 g.)

1. H. W. Foote and J. K. Vance, J. Amer. Chem. Soc., 1935, **57**, 845.
2. H. W. Foote and J. K. Vance, Ind. Eng. Chem., Anal. Ed., 1936, **8**, 119.
3. W. R. Crowell, T. E. Hillis, S. C. Rittenberg and R. F. Evenson, *Ibid.*, 1936, **8**, 9.
4. W. R. Crowell, S. H. Silver and A. T. Spiher, *Ibid.*, 1938, **10**, 80.

Correspondence

Effect of Several Different Alloying Elements on Hardenability of Steel

The Editor, METALLURGIA.

Sir,

Some question has arisen regarding a statement made in my review of the American National Emergency Steels, published in your August, 1944, issue. On page 198 the second paragraph, under the sub-heading "First NE Steels," states that: "The nickel-chromium-molybdenum steel compositions are based on the principle that the effect on hardenability of several different alloying elements of equal hardening power is greater than that of the same total amount of any one of them."

To explain this point to engineers and other non-metallurgists I usually point out that it is analogous to a cocktail, in which it is well known that the effect of small quantities of several different ingredients is more potent than that of a large quantity of a single ingredient. However, the point can be proved mathematically, as shown below :—

Let A and B be two alloying elements for which the relationship between hardenability factor and alloy content is linear, which is true in most cases. Let $H_{(a, x)}$ be the hardenability factor for $x\%$ of A. Let $H_{(b, y)}$ be the hardenability factor for $y\%$ of B. Let k_a and k_b be constants for A and B respectively, which represent their hardening powers.

$$\text{Then } H_{(a, x)} = 1 + k_a x$$
$$H_{(b, y)} = 1 + k_b y$$
$$H_{(a, x + y)} = 1 + k_a (x + y)$$
$$\text{and } H_{(a, b + y)} = (1 + k_a x) (1 + k_b y)$$
$$= 1 + k_a x + k_b y + k_a k_b xy$$

Now if $k_a = k_b$, as for elements of equal hardening power, then $H_{(a, x + b, y)} = 1 + k_a (x + y) + k_a^2 xy$

hence $H_{(a, x + b, y)} - H_{(a, x + y)} = k_a^2 xy$

Similarly,

$H_{(a, x + b, y + c, z)} - H_{(a, x + y + z)} = k_a^2(xy + yz + zx) + k_a^3 xyz$

I have not seen this explanation elsewhere, and it may be of interest to your readers.—Yours very truly,

ROGER F. MATHER,
Chief Metallurgist.

Willys-Overland Motors, Inc.,
Toledo, Ohio, U.S.A.,
September 29, 1944.

The Late Dr. THOMAS SWINDEN

THE announcement of the death of Dr. T. Swinden, on October 27, would come as a shock, not only to his wife, sons and relatives, but to his many friends and, in particular, to members of the iron and steel industry, with which he was intimately associated all his working life. It is common knowledge that he never spared himself in his work, but the heavy strain laid upon him in the war years had already left its mark upon him, as in March of this year he was ordered a complete rest. For slightly more than six months he followed this advice, by which time he had recovered so well that he had resumed part of his former activities with apparently no ill-effects. Indeed, we received a letter from him just a week before he died, advising us that he had recovered sufficiently to commence part-time duty, and that he hoped soon to be in full swing again.

It is probable that the long period of inactivity, so difficult for a busy man to bear in these critical times, had brought about his return to duty sooner than his physical condition warranted ; certainly the fact that he died suddenly, while at the Stocksbridge works of Messrs. Samuel Fox and Co., Ltd., seems to support this view. The shock of his loss, therefore, was all the keener, especially to his family, and also to his staff and colleagues, by whom he was held in such deep and sincere respect ; indeed, it can be said with truth that his staff regarded him with affection. He combined, with undoubted genius and ability, that rare quality of leadership as well as a natural kindliness and tolerance which endeared him to all with whom he came into contact. He was a charming man, who shunned publicity for himself.

His scholastic record is outstanding. Born in Sheffield in August, 1886, he received his initial schooling at Sheffield Central Secondary School, continuing his education at Sheffield University, where he obtained an Associateship in Metallurgy in 1905, and was awarded a Mappin Medal and also a City and Guilds Bronze Medal. Subsequently he won the 1851 Exhibition Scholarship for the years 1906-1908, studying at Sheffield, Stockholm and Upsala. He graduated as B.Met. in 1907 and earned his M.Met. in 1908 ; as a result of further researches the degree of Doctor of

Metallurgy was conferred upon him in 1913. From 1909 to 1913 he was a Carnegie Research Scholar, winning the Carnegie Gold Medal. He was also a Freeman of the Cutlers' Company.

Of his career, only a brief outline can be given here. After some experience with Dr. Longmuir in consulting practice, Dr. Swinden joined Samuel Fox and Co., Ltd., of Stocksbridge, in 1909, as chief chemist, subsequently becoming chief metallurgist, and later works manager and director. In 1932, he relinquished the position of works manager to become Director of Research of The United Steel Companies, Ltd., while still retaining his directorship of Samuel Fox and Co., Ltd., an associate company of The United Steel Companies, Ltd. He was also a director of the Distington Hæmatite Iron Co., Ltd., and of the British Magnesite Corporation, Ltd.

The combination of practical experience in laboratory and works management and in steelmaking, with his scientific training and bias, made Dr. Swinden an outstanding personality ideally fitted for the highly responsible position of Director of Research. The Central Research Department at Stocksbridge, which was his headquarters, bears the hallmark of the care with which he planned it. It contains probably one of the finest sets of equipment to be found in an industrial laboratory in this country, and the same care was devoted to the selection of the senior staff, which, under his guidance, has become a most effective team.

Following his early pioneer work on tungsten and molybdenum steels, Dr. Swinden made very many contributions to technical literature, and these earned for him the much-prized distinction of the Bessemer Gold Medal of the Iron and Steel Institute, the M. C. James Gold Medal of the North-East Coast Institution of Engineers and Shipbuilders, and the Silver Medal of the Institution of Marine Engineers.

Dr. Swinden's activities, however, did not end with his direct duties in the United Steel Companies, Ltd. To keep abreast of current research, and to make a fitting contribution to the common pool of knowledge, he was a member of the Iron and Steel Industrial Research Council, Vice-President of the Iron and Steel Institute, as well as a member of innumerable joint

committees and sub-committees of the British Iron and Steel Federation and the Iron and Steel Institute, being actually chairman of the following : Heterogeneity of Steel Ingots Committee ; Corrosion Committee ; Oxygen Sub-Committee (now Sub-Committee on Gaseous and Non-Metallic Inclusions) ; Alloy Steels Research Committee ; Physical Chemistry of Steelmaking.

He was one of the founder members and a member of Council of the new British Iron and Steel Research Association, which is to undertake the reorganisation of co-operative research in the iron and steel industry.

Other work included the chairmanship of the Open-Hearth Refractories Joint Panel of the British Iron and Steel Federation and the British Refractories Research Association ; member of Council of the British Refractories Research Association ; vice-president of the Refractories Section of the Ceramic Society ; member of the B.R.R.A. Blast Furnace Refractories Panel ; member of Council and of the Research Council of the Institute of Welding and chairman of the Weldability of Ferrous Metals Committee, as well as of the Committee on Physical Metallurgy of Alloy Steel Welding ; chairman of the Alloy Steels Association Technical Committee; vice-president of the British Cast Iron Research Association ; member of the J/E Sub-Committee on Steels for High Temperatures and Creep Properties of the British Electrical and Allied Industries Research Association ; member of the Open Hearth Committee, of the Rolling Mill Committee, and the Rolling Mill Research Sub-Committee of the British Iron and Steel Federaton ; member of the Research Committee and of the Pressed Steel Research Committee of the Institution of Automobile Engineers ; Fellow of the Royal Aeronautical Society and of the Institute of Physics ; past president of the Sheffield Metallurgical Society and of the Society of Engineers and Metallurgists ; vice-president of the Institute of British Foundrymen. For a number of years Dr. Swinden was a member of Council of Sheffield University, as well as several of its committees, including the Appointments Board.

A considerable amount of time was spent by Dr. Swinden in connection with the many committees of the British Standards Institution, of which he was also a Council member, whilst his war-time activities included the following Ministry of Supply and other Governmental Committees :—Chairman of the Metallurgy Committee of the Scientific Advisory Council ; chairman of the Technical Advisory Committee of the Special and Alloy Steels Committee ; chairman of the Aero-Components Sub-Committee ; chairman of the Tank Armour Welding Panel (D.T.D.) ; member of the Tank Armour Electrode Technical Committee (D.T.D.) ; member of the Panel of Consultants to the Research Department (representing Metallurgy); member of the Admiralty Chemical Advisory Panel Group V (Metallurgy) ; member of the Gun Barrel Life Panel ; member of the Iron and Steel Technical Committee ; member of the Advisory Council on Scientific Research and Technical Development ; member of the Basic Furnace Linings Committee ; member of the Tank Armour and Aircraft Sub-Committees of the Armour and Bullet Proof Technical Committee ; member of the Controller's Technical Committee ; member of the 1943 Metallurgical Mission to the U.S.A.

We sympathise with Mrs. Swinden and her sons in having to bear such a great loss. All who knew him or were familiar with his work will appreciate that Britain and, in particular, his native city, can ill afford to lose such a man, who combined so admirably outstanding technical ability with leadership, and yet preserved a most charming disposition.

An Appreciation

By K. HEADLAM-MORLEY,
Secretary of the Iron and Steel Institute.
Abridged

Dr. Swinden was at the time of his death the leading metallurgist in the British iron and steel industry. He knew more and he had accomplished more—he was a leader in more directions—than others. A few—two or three, perhaps—of his contemporaries were gifted with a more brilliant brain. His was a massive and well-balanced intellect. He tried to discover the facts and to consider all the relevant evidence before reaching his conclusions. Above all he despised short cuts to knowledge and thought it dishonest to try to save himself the trouble of thinking.

Dr. Swinden's outstanding characteristics were indeed his modesty and his intellectual and moral honesty. These were the secrets of his great influence and of the very real feelings of respect and affection with which he was regarded. One of the most modest of men, he did not suffer from false modesty and could thus express himself with the simple clarity which convinces ; this made him a good lecturer and his written work was admirably concise. He never attempted to be eloquent but when deeply moved eloquence came to him, and those who heard him speak of the late Dr. Hatfield in the Committees whose work they had so largely shared will long remember his moving tributes.

His dislike of shams, his complete lack of pretentiousness was apparent in every aspect of his living. This is no place in which to do more than touch on his family life but to omit any reference would be to ignore what was for him the side of life which had most to offer. His pleasure in the successful careers which his two sons are making for themselves was very real and his gratitude to his wife, above all for her devoted care during the recent months of illness, was very touching. Those who had the privilege of visiting his unpretentious but beautiful house on the outskirts of Sheffield realised his deep joy in nature and were privileged to obtain a brief insight into the simple happiness of his home. Realisation of what they themselves have lost only serves to deepen their appreciation of the far greater loss which his family has sustained.

Younger men will in time grow to fill the several posts which he held, but we may well have to wait many years before another man comes to fill a similar position in the industry. His experience was exceptionally wide. He could visualise the problems of coke oven and blast-furnace managers, as well as of those who make steel. He considered it a part of his duties to help in solving the problems of production just as much as to contribute towards the understanding of the factors which improve the quality of the product. He was as interested in such cost saving questions as improved refractories and life of ingot moulds as in the constitution of alloy steels. We had hoped that the rest imposed by doctors since the Spring had restored his health . . . Now he, too, has succumbed in a gallant attempt to do more than man could do to further his country's welfare in time of war.

Corrosion of Galvanised Coatings and Zinc by Waters containing Free Carbon Dioxide

By L. Kenworthy, M.Sc., A.R.C.S., and Myriam D. Smith, B.A.

(British Non-Ferrous Metals Research Association).

Premature failures in galvanised cold- and hot-water tanks led to an investigation of one of the controlling factors of corrosion of such tanks—namely, the free carbon dioxide content of the water. Conductivity water, a hard public supply water, and a mixture of the two were tested at room temperature, and the hard water was tested also under conditions approximating to those in domestic hot-water systems. Various carbon dioxide contents were artificially maintained, and both zinc and galvanised mild steel were tested under each condition. The report of this investigation and the results obtained are given in the Journal of the Institute of Metals,* from which this article has been extracted.

AMONGST the conditions which govern the corrosion of galvanised steel and zinc by natural waters are the hardness, the free carbon dioxide content, and the temperature of the water. The present investigation was undertaken to determine the effect on corrosion rate of variation in these three factors separately and together. In preliminary work using conductivity water, two grades of zinc sheet, with cast, rolled, and emeried surfaces, were tested in addition to the galvanised mild steel, but the composition and surface finish of the zinc were found to have so little effect on the rate of corrosion that in the later tests only one grade of zinc was used (that having a cleaned rolled surface). The work is described in two sections, dealing with cold and hot water respectively.

Many workers have studied the corrosion of zinc in distilled and natural waters containing various amounts of carbon dioxide. Bauer and Schikorr[1, 2] found that, in distilled water, the loss in weight of zinc decreased with increasing carbon dioxide content, and attributed this to the production of a protective film on zinc in waters rich in this gas. They observed no marked differences between the rates of corrosion of refined and electrolytic zinc in carbonated water. This view is supported by Taboury and Gray,[3] who found that at low carbon dioxide concentrations, specimens were completely corroded, while at higher carbon dioxide concentrations, a protective coating was formed which proved resistant to the action of water saturated with zinc bicarbonate.

A directly opposed view is held by many other workers. Thus, Bengough and Hudson,[4] using 99·97% zinc, found that the corrosive action of distilled water was greatly intensified when it was saturated with carbon dioxide, and Heyn and Bauer[5] reported increased corrosion of galvanised ware in waters relatively high in carbon dioxide.

Sale and Badger[6] also found greatly increased corrosion on raising the carbon dioxide content of an otherwise harmless tap water.

Many workers have shown that the corrosion of zinc in water reaches a maximum at some temperature between 60° and 70° C. Cox,[7] using aerated distilled water, found maximum penetration at about 65° C., which he attributed to a change in the nature of the

corrosion product at about 53° C. He did not, however, investigate the influence of carbon dioxide on this maximum. Grubitsch and Illi[8] found a maximum at 60° C., in unspecified water, as did Maconochie,[9] using water high in carbon dioxide (pH 5·2). Richards[10] cites a case in which the corrosion of a cold cistern is said to have been accelerated by its proximity to the hot tank. The water was high in carbon dioxide and sodium chloride, and the increased temperature liberated more carbon dioxide. Schikorr[11] has reported a reversal of polarity between zinc and iron above 70° C.; unpublished work by the Association confirms this reversal.

From this survey of previous work it will be obvious that there is no clear evidence as to the effect of carbon dioxide on the corrosion of galvanised coatings and zinc in either hot or cold water.

TESTS IN COLD WATER
(By L. Kenworthy)

All specimens were $3 \times 1·7$ cm. with a hole in the centre near the top edge and each was suspended vertically in a 500-c.c. flask containing 300 c.c. of water. Tests were made in conductivity water, in a hard supply water, and a mixture of equal quantities of both these waters. The carbon dioxide content was varied as shown in Table I, which also gives a typical analysis of the hard supply water. The carbon dioxide was brought to the required concentration by bubbling various mixtures of carbon dioxide and air through the waters overnight. The concentration was maintained after the specimens had been inserted by passing the gas continuously over the surface of the water. Specimens were transferred to freshly saturated water after alternate three- and four-day periods.†

A list of the materials tested in the various media is given in Table II. The galvanised specimens were cut from a hot-dipped sheet.

All specimens except the zinc-iron alloys were tested in duplicate, and all were cleaned with a paste of calcium hydroxide and degreased with acetone before weighing prior to immersion.

A second series of tests was carried out to determine

---

* October, 1944, pp. 463–489 (vol. LXX).

† Tests have shown that the waters saturated with air-carbon dioxide mixtures up to at least 5% carbon dioxide by bubbling overnight are always saturated with respect to oxygen and the concentration of dissolved oxygen is not appreciably different from that of water saturated with pure air even with 5% carbon dioxide mixture.

TABLE I. CORROSIVE MEDIA.

Water.	Free CO₂ Content, Parts/10⁵.	Analysis of Hard Supply Water. Constituent, Parts/10⁵.	
1. Conductivity* (cold) ...	0·06 0·08 0·8 3·6	Free CO₂ .... Chlorine as chloride Sulphuric anhydride Temporary hardness Permanent hardness Nitrogen (as nitrate) Lime .... Magnesia .... Total solids .... Copper .... Iron (as ferric oxide)	0·33 3·1 2·97 22·2 4·4 6·24 14·1 0·9 40·2 0·0025 to 0·007† 0·003
2. Hard supply (cold)	0·0 0·4 1·6 3·4 30 79		
3. Mixture of 1 and 2 (cold) in equal proportions.	0·0 0·5 1·8 3·7 35 90		
4. Hard supply (hot)	0·0 0·56 1·02 2·02 3·50 6·20		

* This water was prepared to give a conductivity of less than 0·1 × 10⁻⁶ mhos when in contact with purified air.
† The copper content was found to vary from time to time.

TABLE II. MATERIALS INVESTIGATED IN VARIOUS MEDIA.

Medium.	A. Zinc Specimens.			B. Zinc-Iron Alloys, % Iron.	C. Hot Galvanised Coatings, Weight of Coating, Oz./Sq. Ft.²	
	Grade, %.	Condition.	Surface Treatment.		One Side.	Reverse Side.
1. Conductivity water (cold)	99·99 Zn 99·99 Zn 99·99 Zn 99·99 Zn 0·86 Pb	Rolled Cast Rolled Cast Rolled	Unprepared „ Emeried to 00 „ „ Unprepared	None	0·40	0·52
2. Hard supply water (cold)......	99·99 Zn	Rolled	Unprepared	None	0·44 Also specimens electro-lytically stripped on one side to leave— 0·4 0·3 0·2* 0·1*	0·53
3. Equal proportions of 1 and 2 (cold).	99·99 Zn	Rolled	Unprepared	4·8 7·6	None	
4. Hard supply water (hot).......	0·1 Pb	Rolled	Unprepared	None	0·8	0·8

* Remaining coating entirely alloy layer.

the corrosion resistance under these conditions of the different layers of a hot-galvanised coating, the specimens being electrolytically stripped on one side to leave various amounts of coating. The stripped side only was tested, the other side being lacquered. These specimens were tested only in the hard supply water containing 3·4 parts/10⁵ of free carbon dioxide.

Analysis of the waters for zinc was carried out as follows : A suitable quantity of solution in a Nessler tube was neutralised with sodium bicarbonate saturated with carbon dioxide and then made up to 100 c.c. with distilled water. 5 c.c. sodium diethyl-dithiocarbamate were added and the zinc estimated colorimetrically after stirring.

Free carbon dioxide was estimated by titration with N/20-sodium carbonate, using phenolphthalein as indicator.

At the end of the tests, the specimens were reweighed after cleaning with 5% acetic acid to remove scale and corrosion product. Microscopical examination was then carried out and the depth of pitting was measured. A final weighing was made after the remaining coating had been stripped from the galvanised specimens by 5% sulphuric acid containing 0·2% arsenious oxide as

inhibitor, and the attack of the coating and the basis metal were calculated.

Results

(a) *Appearance.*—Specimens in conductivity water containing 3·6 parts/10⁵ free carbon dioxide differed markedly from specimens in the other solutions. These specimens assumed a brightly etched appearance which they retained until the end of the test, while the latter quickly became coated with white nodules of corrosion product. The cut edges of the galvanised specimens showed traces of rust after eight days in the solutions containing 0·06 and 0·08 part/10⁵ free carbon dioxide and after 18 days in the solution containing 0·8 part/10⁵ free carbon dioxide, while in the 3·6 parts/10⁵ free carbon dioxide solution no edge rust was visible at het end of the test. The specimens in the solution poorest in carbon dioxide showed a small rust spot on one face of each specimen after 46 days.

Examination of the cleaned specimens revealed that the attack caused by solutions containing the lowest concentration of carbon dioxide (0·06 and 0·08 part/10⁵) was confined to a number of pits. The solution containing 0·8 part/10⁵ produced a much larger number of extremely small pits and some general surface attack. The highest carbon dioxide solution (3·6 parts/10⁵) had given rise to a uniform attack with almost complete absence of pits. Purity and surface condition of zinc appeared to have no effect on behaviour. The galvanised specimens, however, showed a marked difference from the zinc materials in the solution low in carbon dioxide; no conical pits were observed, the attack being confined to shallow cavities which appeared as dark patches.

The behaviour of zinc specimens in the hard supply water and that in the mixed water were similar, but differed considerably from that in conductivity water. There was only a slight tendency for the attack to become more general with increase in carbon dioxide content, the depth of pitting being little greater in the absence of carbon dioxide than in waters containing 3·7 parts/10⁵. The rate of pitting, however, was approximately only one-eighth of that obtained in conductivity water at the lower concentration of carbon dioxide, but was slightly greater than that recorded in conductivity water at the highest concentrations of carbon dioxide.

It is interesting to note that the resistance of the zinc-iron alloys to pitting in the hard and mixed water is considerably greater than that of pure zinc.

(b) *Quantitative Measurements.*—The results are tabulated in the original report. Fig. 1 shows the uniformity of attack of zinc with time, the figures plotted being the mean of those obtained in the hard and mixed waters. Figs. 2 and 3 show the zinc going into solution and the total attack (sum of zinc in undissolved corrosion product and in solution) under the various conditions.
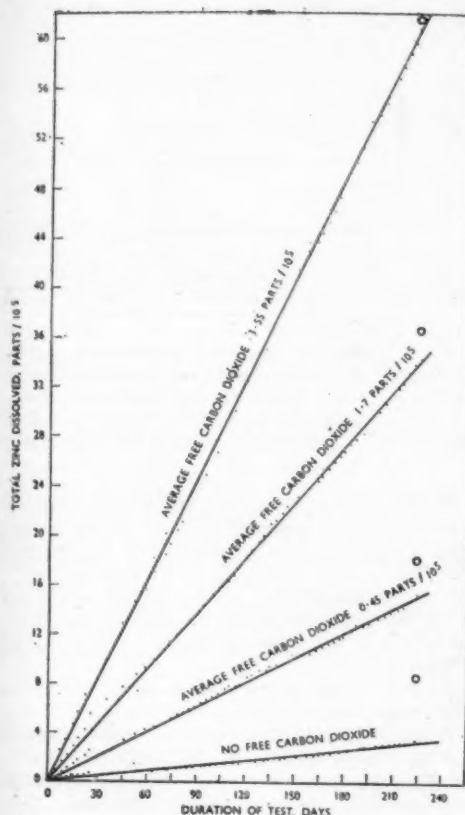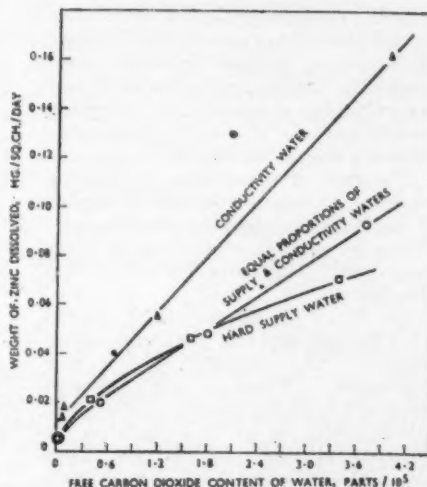
Fig. 1.—Dissolution of zinc by waters containing free carbon dioxide. (Mean results of tests on zinc specimens in supply water and equal parts of supply and conductivity waters at 18° C.). Total attack of zinc shown thus : O.

Fig. 2.—The effect of free carbon dioxide in different waters on the dissolution of zinc. (Average rates over 56 days at 18° C.).

calcium bicarbonate in the water. In waters of low carbon dioxide content, this is liable to be precipitated as a protective carbonate scale on the zinc, but with higher carbon dioxide contents this precipitation will not occur and the dissolution of zinc proceeds unhindered.

The relationship between zinc dissolved and carbon dioxide content (Fig. 2) is linear for pure water and roughly so for mixed water after an initial deceleration ; in the hard water it shows a continuous deceleration similar to that for total attack. This illustrates clearly the reduction of attack of zinc by intentional additions of hardening constituents to a soft water.

It was found that the rate of dissolution of zinc in the mixed and hard supply waters remained uniform over a period of 240 days. This is shown by the data plotted in Fig. 1, where the figures for the amount of zinc dissolved are the mean values for the observations in both kinds of water. Minor deviations are attributed to temperature variations and times of changing of the

Discussion of Results

(a) *Zinc Specimens.*—Fig. 3 shows that, in all three waters, the total attack of zinc increases with increasing carbon dioxide content, and in the mixed water the relationship is linear. In the hard water, however, the increase in rate of attack with rising carbon dioxide content decreases as the carbon dioxide increases, causing the curves for hard and mixed waters to cross at 2 parts/10^5 of carbon dioxide. This is probably due to the simultaneous action of two corrosive agents, the carbon dioxide content and the concentration of salts (other than carbonates) in the water. The greater attack in conductivity water is explained by the complete absence of protective scale-forming carbonates. In the hard water, free from carbon dioxide, the salt concentration is the only factor operating, and the attack is greater than in mixed water. With rise in carbon dioxide content, however, the effect of salt concentration becomes negligible, and the mixed water causes greater attack.

It is shown that the percentage of attacked zinc passing into solution also increases with rise in carbon dioxide content, particularly in conductivity water (see Fig. 3). This is due to the fact that at low concentrations of carbon dioxide in conductivity water the corrosion product is probably basic zinc carbonate, whereas at higher carbon dioxide concentrations the product is zinc bicarbonate. The bicarbonate is more soluble and less protective than the basic carbonate, and attack proceeds steadily, leaving the metal in the brightly etched condition. In the case of the two harder waters, the mechanism is similar, but modified by the presence of
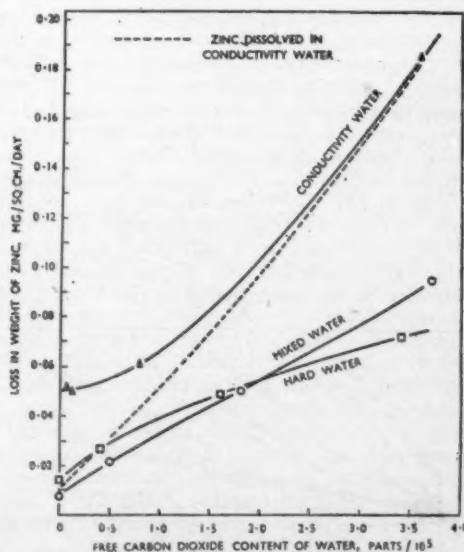

Fig. 3.—The effect of free carbon dioxide in different waters on the attack of zinc (18° C.).

water. The greatest attack takes place in the first 36 hours, after placing the specimens in fresh solution ; consequently, when changing the water was unavoidably delayed, the resulting longer periods showed a somewhat reduced rate of dissolution of zinc.

The rate of penetration by pitting in the solutions low in carbon dioxide is much greater than the rate of penetration by general solution in the water containing $3 \cdot 6$ parts/10^5 of carbon dioxide.

(b) *Zinc-Iron Alloys.*—With regard to total attack, the zinc-iron alloys behaved very similarly to the zinc specimens. There is not sufficient evidence from the few specimens tested for any opinion to be formed on the relative resistance of the two alloys containing $4 \cdot 8$ and $7 \cdot 6\%$ iron, respectively, although the latter may be slightly superior. The resistance of these alloys to pitting, however, is considerably greater than that of pure zinc, as pointed out in Section 2 (a) above. It appears, therefore, that (other considerations apart) where zinc suffers a severe pitting type of attack (e.g., in soft water low in carbon dioxide, or in water of pH $6 \cdot 8$-$9 \cdot 5$ with a low carbonate/carbon dioxide ratio), coatings composed entirely of zinc-iron alloy should be superior to ordinary hot-dipped coatings. These in turn should be superior to electro-galvanised coatings, from which the alloy is entirely absent.

(c) *Galvanised Specimens.*—The final results obtained on the galvanised specimens are tabulated ; they show a difference between the behaviour of the galvanised steel and the zinc specimens in conductivity water with the two lowest carbon dioxide contents. Although the total weights of metal attacked, and also the amounts of zinc passing into solution, were similar, the galvanised steel did not pit at the same rate as the zinc ; the average depth of pits on the galvanised specimens was $0 \cdot 01$ mm. (with a maximum of $0 \cdot 035$ mm.), compared with an average of about $0 \cdot 1$ mm. (and a maximum of $0 \cdot 23$ mm.) in the case of the zinc specimens. The rate of pitting of the galvanised material was, however, rapid enough to cause penetration of a coating of about $0 \cdot 5$ oz./ft.^{2} in 46 days. Since no significant difference was obtained between the various zinc specimens, this phenomenon is not due to the difference in structure or surface condition. It is possible that, when a pit has penetrated through the outer zinc in a galvanised specimen and exposed the alloy layer and later the basis metal, the rate of penetration is decreased owing to the lower solution
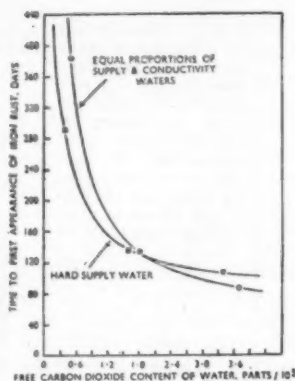
Fig 4.—Influence of free carbon dioxide in waters on the life of galvanised coatings ($18°$ C.).
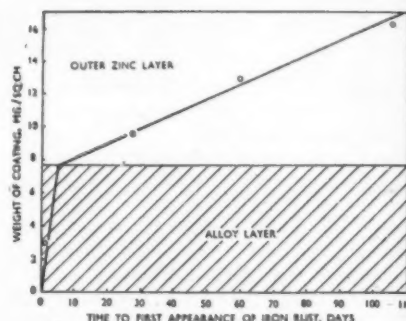
Fig. 5.—Relative electrochemical protection of steel by zinc and alloy layers of a galvanised coating. (Hard supply water : 3-4 parts/10^5 CO_2 at 19 C°.)

potential of the exposed material, which thus becomes cathodic to the zinc and causes the pits to spread instead of penetrating further. This is confirmed by the fact that similar results were obtained in all waters.

The rate of penetration by pitting in the water low in carbon dioxide is greater than the rate of penetration by general attack in the water containing $3 \cdot 6$ parts/10^5 of carbon dioxide.

The amount of zinc passing from galvanised specimens into the solutions containing $3 \cdot 6$ and $0 \cdot 8$ parts/10^5 of carbon dioxide remained approximately constant throughout the tests, but with the solutions low in carbon dioxide the rate of zinc dissolution from the galvanised specimens fell markedly with time from about $0 \cdot 5$ part/10^5 in the first four-day period to about $0 \cdot 05$-$0 \cdot 1$ part/10^5 in the last.

A graph showing the relationship between coating life and carbon dioxide content for the hard and mixed waters is given in Fig. 4. Unfortunately, the figures for the specimens in conductivity water are not available, as the tests were stopped after 56 days, when only the specimens in the solution containing $0 \cdot 05$ part/10^5 of carbon dioxide had shown rust spots on the face. The fact that none of the other specimens had rusted at 56 days seems to indicate that the curve for conductivity water slopes the opposite way to those for the other two waters. It would be unwise, however, to draw any definite conclusion from this single result. In both the hard and mixed waters, the life is seen to decrease with increasing carbon dioxide content, but not at the same rate. As with zinc, the two curves cross at about 2 parts/10^5 of carbon dioxide. The values obtained in
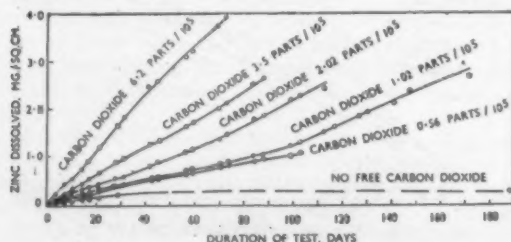
Fig. 6.—Effect of free carbon dioxide on the dissolution of zinc in hot hard supply water.
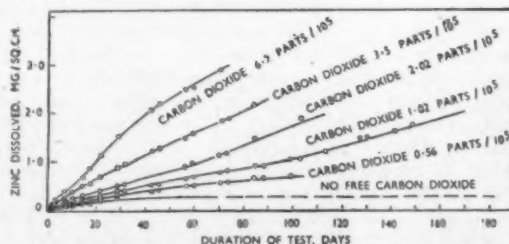
Fig. 7.—Effect of free carbon dioxide on the dissolution of zinc from galvanised coatings in hot hard supply water.
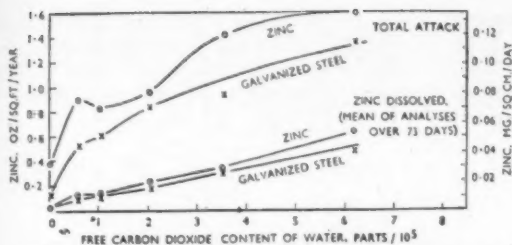
Fig. 8.—Effect of free carbon dioxide on the total attack and dissolution suffered by galvanised coatings and zinc in hot hard supply water.

Fig. 9.—Zinc in adherent corrosion product.

hard water saturated with 30 and 100% carbon dioxide atmospheres have been omitted from Fig. 4, in order that the results for the range most important, from a practical standpoint (i.e., up to 4 parts/10^5 carbon dioxide) shall be represented on a reasonably large scale. It was found, however, that the life with the 30% carbon dioxide atmosphere was somewhat shorter than that with the 100% carbon dioxide, due, presumably, to the relative absence of oxygen in the latter case. In these two solutions, the penetration of the coating was not immediately obvious, as no visible rust was formed, the specimens quickly turning black and exhibiting little further change in appearance. Failure was deemed to have occurred when the iron content of the water suddenly rose, causing interference in the analysis for zinc.

The results of tests showed clearly that the corrosion of zinc ceases as soon as rusting of the basis steel sets in. This is borne out by the sudden drop in zinc content of the water after the appearance of iron rust on the specimen.

The results obtained with the partly stripped galvanised specimens are given. As would be expected, the length of life of the coatings decreased with reduction in thickness, but the exact relationship between these two values is of great interest, as will be seen by reference to Fig. 5. From this it is clear that the electrochemical protection given to the steel by the alloy layer is negligible ; further, the protection afforded by the outer zinc layer is directly proportional to its thickness. These points confirm the results of the tests on zinc and galvanised steel previously described and support the conclusions regarding the effects of thickness and composition on coating life.

TESTS IN HOT WATER
(By Myriam D. Smith)

(a) *Protection of Cut Edges.*—Preliminary tests showed that galvanised specimens $3 \times 1 \cdot 7$ cm. with bare steel cut edges, in contrast to those tested in cold water, showed rust at the point of suspension and at points on the edges after only three days in tap water (free carbon dioxide content $0 \cdot 33$ part/10^5, combined carbon dioxide content 17 parts/10^5) maintained at 70°–80° C. To overcome this difficulty, the cut edges were protected by a Bakerlite varnish dried at 135° C., which proved insoluble in acids, potassium cyanide, alcohol, and acetone, all of which were used in the cleaning and stripping processes. The resistance of the varnish to hot water was generally good.

(b) *Change of Carbon Dioxide Content on Heating.*—Flasks completely filled with tap water of different free carbon dioxide contents ranging from $0 \cdot 69$ to $7 \cdot 98$
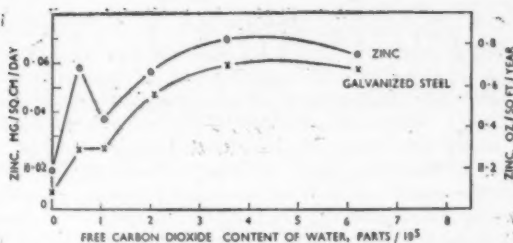
parts/10^5 and fitted with capillary expansion tubes were heated to 75° C. for 24 hours. The reduction in carbon dioxide content after heating averaged about 50% but was not strictly reproducible. When the water was allowed to stand in the laboratory at room temperature in uncovered wide-mouthed vessels, its carbon dioxide content fell by 85% in 24 hours. It was therefore decided that the tests should be done in entirely filled flasks with small overflow funnels and that all estimation of free carbon dioxide should be made in the cold, before the tests began. The water was changed after alternative three- and four-day periods, and the flasks were allowed to cool overnight. The total time at the maximum temperature therefore averaged 21 hours, and at the end of each period the carbon dioxide content was probably very small.

Experimental Procedure

(a) *Materials Used.*—The specimens were of the same shape and size as in the tests in cold water and were also tested in duplicate. Tables I and II give the materials investigated, the analysis of the water, and the concentrations of carbon dioxide used. The method of aeration, the cleaning procedure, analysis methods, and times of changing the water were the same as those employed in the cold tests, but the detailed procedure and method of suspension of the specimens varied somewhat.

(b) *Method of Suspension and Changing of Water.*—Specimens were suspended from glass hooks in flasks containing 500 c.c. water and fitted with an expansion funnel. This device enabled the water which overflowed from the flask during the heating period to draw back without introducing air. The ratio area of zinc/volume of water under these conditions approximates to that in 30-gal. galvanised tanks.

(c) *Temperature.*—The flasks were immersed to within 2 in. of the top of the neck in a water bath maintained at 85° C. for 6 hours daily and allowed to cool to 35° C. overnight.

(d) *Cleaning and Stripping.*—Specimens were cleansed by immersion for a short time in 5% acetic acid and brushing with a stiff bristle brush. Further brushing in hot water or rubbing with a rounded piece of wood was continued until substantially all the corrosion product was removed. Final traces were removed by cleaning cathodically in 10% potassium cyanide using an iron gauze anode and a current of $1 \cdot 5$ amps. The remaining coating was stripped from the specimens by inhibited acid, as for the tests in cold water.

(e) *Criterion of Failure.*—Galvanised specimens were deemed to have failed when a spot of loose red rust appeared on the face of the specimen.

Results

(a) *Appearance.*—Attack in all cases was by pitting, mainly at the centre of cups of white corrosion product or scale which formed at the bases of gas bubbles on the specimens. Very often the bubbles were removed when the water was changed, but fresh bubbles tended to appear in the same places as before. Scale precipitated from the water, as well as corrosion product, accumulated on the specimens. On the zinc specimens the scale formed hard nodules, distinct from, but additional to, the bubble cups, and was in general more voluminous than the scale on the corresponding galvanised specimens. Also, the corrosion product adhering to the zinc specimens increased with carbon dioxide content of the water. In contrast the amount of scale and corrosion product on the galvanised specimens appeared to be least in the waters containing most carbon dioxide.

The above observations were made after five weeks, but apart from general darkening of the galvanised specimens the appearance did not thereafter show much change until failure.
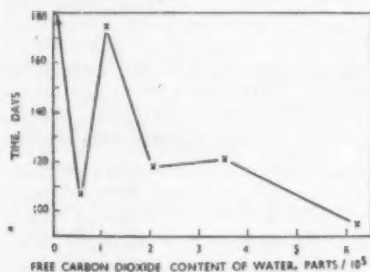

Fig. 10.—Effect of free carbon dioxide on the time of rusting of galvanised coatings in hot hard supply water.

(b) *Quantitative Measurements.*—Figs. 6 and 7 show the relationship between the zinc dissolved and the time of immersion for zinc and galvanised specimens respectively. The tests were continued either until the specimen failed or until the rust from edges which became exposed during the test so contaminated the solution that further zinc estimation became impossible.

The mean attack, calculated from the total zinc dissolved and in the corrosion product, and from the total time, is shown in the upper part of Fig. 8. The lower part of the figure shows the mean attack by dissolution of zinc only, and Fig. 9 the mean amount of adherent corrosion product produced per day over the whole period. The curves in the lower part of Fig. 8 show that the attack by dissolution increases with increasing carbon dioxide content, approximately in direct proportion to the carbon dioxide content above a figure of about $1 \cdot 0$ part/10^5. The total attack passes through a maximum at $0 \cdot 56$ part/10^5 and a minimum at 1 part/10^5 carbon dioxide. Both mean attack and zinc dissolved are again considerably greater in the case of zinc than in that of galvanised steel. Fig. 9 again shows a maximum at $0 \cdot 56$ part/10^5 and a minimum at 1 part/10^5 carbon dioxide, and above this figure the corrosion product adhering to the specimens increases with carbon dioxide content up to about $3 \cdot 5$ parts/10^5 and then falls off. Again the attack of zinc is greater than that of galvanised steel.

(c) *Rusting of Galvanised Specimens.*—Figs. 10, 11 and 12 show the time that elapsed before rusting of the face of the specimen was observed, the percentage coating remaining when rusting occurred, and the rate of pene-

tration at the point of failure. The last figures were obtained by assuming that the whole of the original coating had been removed at the point where failure occurred. In Figs. 10 and 12 the specimens in water of
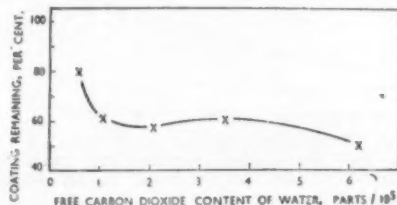
Fig. 11.—Rusting of galvanised coatings in hot hard supply water. Variation of remaining coating at time of rusting with carbon dioxide content of water.

carbon dioxide content $0 \cdot 56$ part/10^5 show minimum time for rusting and maximum rate of penetration, confirming the maximum mean attack and adherent corrosion product at $0 \cdot 56$ part/10^5 carbon dioxide in Figs 8 and 9.

The maximum time for rusting and the minimum rate of penetration at 1 part/10^5 carbon dioxide corresponds to the minimum at 1 part/10^5 carbon dioxide in Figs. 8 and 9. The specimens in water free from carbon dioxide had not failed at 191 days, when the tests were concluded, the coating then remaining being more than 90%. Rusting usually occurred at the centres of the bubble cups.
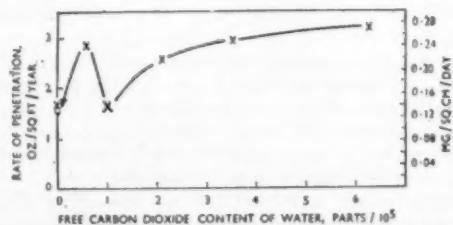
Fig. 12.—Rusting of galvanised coatings in hot hard supply water. Variation of rate of penetration at point of failure with carbon dioxide content of water.

General Conclusions

1. The attack of zinc and galvanised mild steel by conductivity water, a hard public supply water, and a mixture of the two in equal proportions, is, both at 18° and 85° C., in general increased by increasing the original free carbon dioxide content of the waters.

2. In all waters tested, the amount of zinc entering into solution increases progressively with increase in carbon dioxide content, and the corrosion product formed becomes increasingly soluble.

3. In all waters tested, the pitting of zinc is found to be more rapid than that of galvanised coatings.

1 O. Bauer and G. Schikorr. *Z. Metallkunde*, 1934, 26, 73.
2 O. Bauer and G. Schikorr. *Mitt. Materialpruf. Anst. Sonderheft*, 26, 1934, 63.
3 F.-J. Taboury and E. Gray. *Bull. Soc. chim. France*, 1939 (v), 6, 368, 374
4 G. D. Bengough and O. F. Hudson. *J. Inst. Metals*, 1919, 21, 59.
5 E. Heyn and O. Bauer. *Mitt. Materialpruf. Amt*, 1912, 30, 101.
6 J. W. Sale and C. H. Badger. *Indust. and Eng. Chem.*, 1924, 16, 164.
7 G. L. Cox. *Indust. and Eng. Chem.*, 1931, 23, 902.
8 H. Grubitsch and O. Illi. *Korrosion u. Metallschutz*, 1940, 16, 197.
9 J. E. Maconochie. *Trans. Electrochem. Soc.*, 1934, 66, 213.
10 H. F. Richards. *Iron Steel Ind.*, 1928, 1, 185.
11 G. Schikorr. *Trans. Electrochem. Soc.*, 1939, 76, 247.

The Surface Film on Chromium-Nickel 18-8 Stainless Steel

By W. H. J. Vernon, D.Sc., F. Wormwell, Ph.D., and T. J. Nurse.

(*Department of Scientific and Industrial Research*).

The surface film, stripped from chromium-nickel (18–8) austenitic steel, has been studied and the metals present determined by chemical analysis. The experimental work involved and the results obtained are described in a recent report* published by the Iron and Steel Institute from which this article is abstracted.

IMMEDIATELY before the present war the authors carried out work on the air-formed film on iron and mild steel.[1] At that time it was intended to explore the possibilities of a similar technique applied to surface films on "stainless" alloy steels. The experiments described in the present report, using austenitic (18–8) chromium nickel steel, represent a preliminary programme of work, much of which had been completed at that time, but was suspended on account of pressure of more urgent problems. Recent developments in this

of the film from the metal. In the present work it was further found that for this separation to yield a film representing *quantitatively* the oxide present on the metal, it is necessary to exclude both water and oxygen from the system. This led to the technique previously described,[1] in which a solution of iodine in anhydrous methyl alcohol is used as the stripping reagent in an apparatus designed to facilitate the removal of atmospheric oxygen.

Reference should also be made to the anodic method of film stripping developed by U. R. Evans and J. Stockdale.[4] By long anodic treatment of 13% chromium steel these workers obtained, in addition to opaque flakes, a very thin transparent film, carrying striae

TABLE I.
DATA FROM CHEMICAL ANALYSES OF FILMS.

Reference No.	Surface Finish.	Contents of Film,† µg. per Sq. Cm.			Approximate Total Oxides in Film, µg. per Sq. Cm.	Calculated Approximate Film Thickness.‡ A.		Cr/Fe Ratio in Film.
		Fe₂O₃.	Cr₂O₃.	Al₂O₃.		(1).	(2).	
A.—INFLUENCE OF DEGREE OF POLISH.								
22 / 23	Abraded, Ia	2·0 / 2·1	1·4 / 1·5	—	3·5	70	30	0·7 / 0·7
20 / 21	Low-grade polish, Ib.	0·8 / 0·8	2·9 / 3·1	—	3·7–3·9	75	45	3·5 / 3·8
15 / 16	Low-grade polish, Ic.	0·85 / 0·8	3·4 / 3·1	—	4·0–4·2	80	45	4·0 / 3·8
17 / 19	High-grade polish, Id.	0·5 / 0·45	3·7 / 4·2	—	4·2–4·6	85	50	7·2 / 9·3
B. INFLUENCE OF POLISHING MATERIAL (HIGH-GRADE POLISH, II).								
26 / 27 / 30 / 31	Alumina polish ..	1·6 / 1·6 / 1·2 / 1·4	4·1 / 4·2 / 3·5 / 3·3	N.d.§ / N.d.§ / 2·1 / 2·6	7·0–8·0	160	95	2·5 / 2·6 / 2·8 / 2·3
28 / 29 / 32	Chromic oxide polish.	0·8 / 0·6 / 0·6	6·8 / 5·7 / 5·4	—	6·0–7·5	130	75	8·5 / 9·3 / 8·7
C. INFLUENCE OF HEAT-TREATMENT.								
12 / 13 / 14	Low-grade polish, Ic. Heated at 500° C. for 17 hours.	7·4 / 8·4 / 7·2	16·0 / 16·0 / 14·8	—	22·0–25·0	450	265	2·1 / 1·9 / 2·0

† Determined as metal, calculated as oxide.
‡ Values expressed to nearest 5 A. (1) on " apparent " area of specimen ; (2) on estimated " real " area.
§ Not determined.

TABLE II.
APPROXIMATE PERCENTAGE COMPOSITION OF FILMS.

Reference Number.	Surface Finish.	Concentration of Oxide in Film, by Weight, %.°		
		Fe₂O₃.	Cr₂O₃.	Al₂O₃.
A. INFLUENCE OF DEGREE OF POLISH.				
22 / 23	Abraded, Ia	59 / 58	41 / 42	—
20 / 21	Low-grade polish, Ib	22 / 21	78 / 79	—
15 / 16	Low-grade polish, Ic	20 / 20	80 / 80	—
17 / 19	High-grade polish, Id	12 / 10	88 / 90	—
B. INFLUENCE OF POLISHING MATERIAL (HIGH-GRADE POLISH, II).				
30 / 31	Alumina polish	18 / 19	51 / 45	31 / 36
28 / 29 / 32	Chromic oxide polish............	10 / 10 / 10	90 / 90 / 90	—
C. INFLUENCE OF HEAT-TREATMENT.				
12 / 13 / 14	Low-grade polish, Ic. Heated at 500° C. for 17 hours.	32 / 34 / 33	68 / 66 / 67	—

° Values are calculated directly from the data of Table I and expressed to the nearest unit figure without any implication as to the degree of accuracy involved.

field suggest the desirability of placing the results on record, particularly in view of their possible practical implications.

The earliest work on the removal of surface films from ferrous materials was carried out by U. R. Evans[2, 3] who succeeded in stripping films from passive and heat-treated iron by the use of a solution of iodine in aqueous potassium iodine. It was discovered that iodine has the property of attacking metallic iron preferentially along the boundary between metal and oxide, thus permitting (since it has not action on the oxide itself) the separation

representing the original abrasive treatment. Their attempts to obtain the film from austenitic 18–8 chromium-nickel steel yielded a skin containing so much residual metal as to be opaque. The modified (chemical) technique now employed has been found to be applicable to this type of steel, and the film so obtained is believed to be free from contamination. The present paper refers to results obtained from the examination of this film.

The 18–8 chromium nickel steel used in the experiments was supplied, through the kind offices of the late Dr. W. H. Hatfield, F.R.S., in the form of sheet 0·45 mm. thick. The following surface treatments have been examined :

Series I :

    (*a*) Abraded with Hubert No. 1 emery paper in the laboratory.

    (*b*) Ground and polished industrially low-grade polish.

    (*c*) As (*b*), except that the works method followed was such as to give a rather better polish.

    (*d*) Ground and polished industrially high-grade polish (mirror finish).

Note.—It was known definitely that no chromium oxide was used in the polishing by processes (*b*) and (*c*). It is possible that chromic oxide was used in the later stages of (*d*), but unfortunately the point was overlooked until it was too late to be checked with certainty. In order to put the effect of polishing treatment beyond doubt it was decided to carry out a further series of tests on sheet material polished specially for the work (arrangements for which were kindly made by Dr. Hatfield) as follows :

Series II :

    (*a*) High-grade polish (mirror finish), using alumina as the final polishing material.

    (*b*) High-grade polish (mirror finish), using chromic oxide as the final polishing material.

Note.—The degree of polish in (*a*) and (*b*) was, as nearly as could be arranged, identical.

Specimens measuring $5 \times 2 \cdot 5$ cm. were cut from the polished sheets and kept in a desiccator. Immediately before use in a stripping experiment, each specimen was degreased by passing through several baths of pure benzene, and finally " trimmed " with shears to ensure freshly-cut edges (this was necessary for the success of the stripping), the precise dimensions of the specimen being determined after the experiment. The general procedure followed closely that adopted in the previous work.

Results and Discussion

Composition of Films and Surface Condition.—Experimental and calculated data with respect to the composition of the films are given in Tables I and II. Iron, chromium and aluminium, estimated as metal, are expressed as Fe_2O_3, Cr_2O_3 and Al_2O_3, respectively. The last-named, when present, is obviously derived as such from the polishing material. The assumption that iron and chromium are present in the surface film as the respective oxides may be regarded as a reasonable extrapolation from the knowledge of the air-formed film on iron ; it is also consistent with available electron diffraction evidence relating to stainless steel surfaces.[*] Although the possibility cannot be excluded that some unoxidised metal (both iron and chromium) is present,[†] it is reasonable to conclude that the film is made up essentially of the mixed oxides. In Table I these are reported as μg. per sq. cm. of surface area and in Table II as percentages by weight of the total oxide content of the film.

The presence of nickel was detected in all the samples examined, but only in two (Nos. 30 and 31, alumina-polished specimens, Series II), and then without any

margin, was the content sufficiently high to fall within the limits of satisfactory measurement. (As the minimum amount of nickel that can be estimated in a given determination is about 10 μg., this corresponds, taking into account the area of the films employed, to about $0 \cdot 13$ μg. of nickel or $0 \cdot 17$ μg. of NiO per sq. cm. ; alternatively, it represents rather less than 2% of the total oxide content of the film.) For this reason nickel is not included in the Tables but is discussed in the text (*infra*) ; its omission from Table II cannot sensibly affect the approximate percentage values of the major constituents.

It is apparent (*see* Table I, *A*) that the Fe_2O_3 content of the film decreases as the degree of polish increases, *e.g.*, it is 4 times as great in the film from the abraded as from the most brightly polished specimens. (The higher Fe_2O_3 content of films from specimens polished with alumina is discussed later.) On the other hand, there is a marked increase of Cr_2O_3 with increase of polish, irrespective of whether chromic oxide is used in the polishing process. The effect of polishing is brought out most strikingly by considering the ratio of chromium to iron ; $0 \cdot 24$ in the underlying steel, this increases to $0 \cdot 7$ in the film from abraded specimens and to $3 \cdot 8$ with even a moderate (" low-grade ") polish. Although there is some doubt whether or not chromic oxide was used in the final stages of the high-grade polish (Nos. 17 and 19), it is believed that the very great increase in the Cr–Fe ratio to a mean value of $8 \cdot 3$ (the individual value of $9 \cdot 3$ is nearly 40 times greater than the ratio in the basic steel) is entirely consistent with the effect of polish *per se*. This is borne out by the comparatively small increase in the chromium content (*cf.* results from the low-grade polish for which chromic oxide was definitely not used) and the continued marked fall in iron content, which is clearly a characteristic of increasing intensity of polish.

The matter is rendered clearer in Table II, where it is seen that the concentration of chromic oxide in the films, even from the low-grade polish, is as high as 80% of the total oxide, a value that is realised very closely in each of the four separate determinations. Considering the much more advanced stage represented by the high-grade polish, an increase of the chromic oxide content to 90% is no more than would be expected on the basis of polish alone, and no evidence is afforded of any appreciable contribution of chromic oxide from the polishing material. The results (Table I) support the conclusion that a relationship subsists between the efficiency of the polishing and the ratio of chromium to iron in the film.

The low content of nickel in the films is in marked contrast with the enrichment of chromium. To confirm that the technique itself was not responsible for failure to detect any such enrichment of nickel that might, in fact, have occurred, supplementary experiments were carried out on specimens of sheet nickel on which oxide films had been produced by heat-treatment, the amount of nickel in the film being calculated from the equivalent oxygen content as measured by weight-increment. The stripping and subsequent examination of the film were carried out according to the present technique, and satisfactory quantitative agreement was obtained between calculated and observed amounts of nickel.[‡] The

---

[*] T. Tokumitu[3] concluded from the electron-diffraction examination of stainless steel surfaces after heating at different temperatures that the naturally occurring film of oxide in the Fe, Cr_2O_3 form. This confirmed the findings of S. Miyake[4] (using a similar technique) with respect to the presence of Fe_2O_3, Cr_2O_3 solid solution.

[†] In the earlier work[1] it was concluded that a little metallic iron must be present in the thin oxide films produced by heating iron in air. In the present work, the films produced by heating 18–8 chromium-nickel steel appear to carry a greater content of metal (*see* under " Influence of Temperature on Composition of Films "). Further information is clearly required concerning the content of free metal in films produced by polishing as distinct from films produced by heating in air.

[‡] The agreement obtained was precisely consistent with a formula of NiO for the nickel oxide removed. This confirms electron diffraction evidence for the constitution of the oxide film *in situ* on heated nickel[7]. On chromium (700° C.) Miyake[4] found Cr_2O_3 and on Nichrome (700–900° C.) NiO, Cr_2O_3. There are grounds, therefore, for representing as NiO the small amount of nickel oxide found in the stripped film in the present work.

results from two of the alumina-polished specimens in which a determination of nickel in the film was possible indicated that the nickel–iron ratio in the film was just equal to that in the steel ; on the other hand, this ratio was not realised in the films from the other two alumina-polished specimens, nor in the film from the abraded specimens of Series I, where the iron content was sufficiently high for nickel to have been determined had the metallic ratio been maintained. It follows that, whilst the absence of any appreciable enrichment of nickel in the film is quite definite, the evidence does not warrant any conclusion as to the actual proportion of nickel that passes into the film. No case has been found in which the ratio of nickel to iron in the film is measurably greater than that in the metal ; in several cases it is less.*

Relative Thickness of Films.—An estimate of the thickness of the film before stripping was obtained from the total oxide content, assuming Fe_2O_3, Cr_2O_3 and Al_2O_3 to have densities of $5\cdot1$, $5\cdot2$ and $4\cdot0$,† from which the respective contributions to the total volume were derived. The values of film thickness (in Ångstrom units), as given in Table I, column (1), were calculated on the apparent area of the specimen, " thickness " being regarded as the mean of the intercepts made by the film on lines normal to the general plane of the surface. If allowance be made for the greater real area (" thickness " then being regarded as the mean of the intercepts made by the film on lines normal to *small elements* of the surface), it is evident that correspondingly smaller values, approximating more closely to the true thickness of the film, will result. This has been attempted in column (2), where the factors applied to convert apparent to real area are those due to Erbacher,[8] namely, $2\cdot5$ for abraded, and $1\cdot7$ for polished surfaces. Although individual thickness values must be regarded as approximations only, the relative values demonstrate clearly the influence of polishing on film thickness, the film on the most highly polished specimens being at least twice as thick as that on abraded surfaces. (It is probable that a more accurate knowledge of real/apparent area relationships would reveal a greater differentiation in film thickness between the low-grade and high-grade polish.)

Influence of Polishing Material on Composition of Films.—In Series II two groups of specimens were given as nearly as possible an identical degree of polish by means of alumina and chromic oxide, respectively. Considering specimens polished by alumina (Nos. 30 and 31), it is clear from Tables I and II that an appreciable amount of alumina has been forced into the surface during polishing and has become an integral part of the surface film. At the same time the thickness of the film has considerably increased (approximately double the thickness of the high-grade polish film of Series I) and with it the content of iron oxide. Both film thickness and iron oxide content are also considerably greater than (the latter approximately double) the values for the corresponding chromic-oxide-polished specimens. The increased thickness may be in part an effect of temperature (*vide infra*), since it is possible that in the endeavour to obtain a polish equal in brightness to that on specimens polished with chromic oxide, a greater amount of work was expended with consequent greater rise of surface

temperature. The marked reduction in chromic oxide content as compared with the films from chromic-oxide-polished specimens is consistent with the displacement of chromic oxide by the intrusive alumina. This is illustrated by the percentage values in Table II. Thus, considering films from chromic-oxide-polished specimens, the content of Cr_2O_3 is in each case 90%, in agreement with each of the high-grade-polish films of Series I. For the reasons already discussed, it is unlikely that this content was appreciably influenced by the use of Cr_2O_3 in polishing, and the value of 90% is almost certainly characteristic of the high degree of the polish. It would appear that the rate of supply of chromium from the metal is sufficient to maintain the concentration of chromic oxide in the film at the maximum value in the neighbourhood of 90% ; this value is therefore not exceeded when chromic oxide is also supplied extraneously.‡ On the other hand, when alumina is forced into the film from outside, the concentration of chromic oxide is necessarily reduced. In fact, it is reduced (Table II) by a greater amount (about 42%) than the amount (about 34%) of alumina taken up, the difference being due to a simultaneous increase of ferric oxide.§ This may be brought about by a greater solubility of Fe_2O_3 in Al_2O_3 as compared with Cr_2O_3, but this is speculative in the absence of information on the mutual solubilities of the several oxides in the flowed layer.

Influence of Temperature on Composition of Films.— For the very limited experiments on the influence of temperature (results under C in Tables I and II), specimens having the low-grade polish Ic were heated in air in a thermostatically controlled furnace at 500° C. for 17 hours. As the mean increase of weight due to oxygen taken up during heating ($4\cdot4$ μg. per sq. cm.) fell considerably short of the oxygen increase calculated from metal content, it may be concluded that an appreciable amount of iron or chromium (or both) is present as metal ; some of the iron, moreover, may be present as FeO. Further work is necessary to settle these points. From the present point of view, the outstanding feature is that, although the thickness of the film has increased by some 500%, the chromium–iron ratio has fallen by about 50% of its original value. Making due allowance for the arbitrary temperature conditions (moderate temperature with prolonged heating period), it is of interest to compare the effect of this heat-treatment with the influence of polish, which, besides a considerable rise of surface temperature, must involve a certain amount of surface flow. In each case there is enrichment of chromium in the film as compared with the metal, but it is much more marked for polishing than for simple heat-treatment. This is shown by the relevant data of Table I, C. Thus, heat-treatment has produced a film of thickness greater than 200 A, with a chromium–iron ratio of about $2\cdot0$, whereas polishing alone (A, Nos. 17 and 19) yielded a chromium–iron ratio some 4 times greater in a film of only a fifth of the thickness. The results suggest that the effects produced by polishing, *e.g.*, a high chromium–iron ratio in a very thin surface film, cannot be explained in terms of surface temperature alone. No doubt the far higher temperatures reached transiently in the process of polishing would facilitate

---

* It is noteworthy that Miyake,[9] in his electron-diffraction study of films *in situ* on heated surfaces of iron, chromium, nickel and their alloys, found in the case of iron-nickel alloys a complete absence of nickel in the film, which consisted of Fe_3O_4. On the other hand, Nichrome gave a film of " pure $NiCr_2O_4$."

† Values taken from International Critical Tables.

‡ Naturally, some of the chromic oxide found in the film from the chromic-oxide-polished specimens may be expected to come from the polishing materials, but in that event the contribution from the oxidation of chromium in the steel must be correspondingly reduced.

§ This statement assumes that iron is present entirely as Fe_2O_3 ; an alternative explanation is obviously that some is present as metallic iron or as FeO (*see* under " Composition of Films and Surface Condition ").

diffusion in the surface layers. There would seem to be little doubt, however, that the major distinction is that of surface flow in the one case and its absence in the other, the increased mobility allowing greater freedom for the competing metals to take up oxygen according to their respective reactivities. It is significant that the order (qualitatively) in which the oxides appear in the film is that of the corresponding free energies of formation, viz., Cr_2O_3, -249 ; Fe_2O_3, -179 ; NiO, $-52*$ A quantitative agreement with this order would not be expected, since other factors must intervene to control the oxidation rate. It is suggested that the great predominance of Cr_2O_3 may be accounted for by the selective oxidation of chromium according to the principle described by Thomas and Price.[10,11] This depends on the supply of atmospheric oxygen at the metal surface being severely restricted as, for example, when an alloy is heated in an almost inert atmosphere ; the oxidation of the more reactive constituents is thereby favoured even when it is present in minor proportion in the alloy. In the polishing of stainless-steel surfaces it may be well that such conditions will operate, bearing in mind the intimate contact that must be maintained between the metal and the polishing medium, especially during the periods when surface flow is taking place.

Effect of Polishing and of Polishing Material on Electrode Potential of Surface Film (in situ).—Electrode potential measurements on the stainless steel sheet, immersed in N/200 sodium chloride solution exposed to air have been used to compare the passive properties before and after stripping the surface film, and to examine differences of passivity produced by different polishing methods. Specimens measuring $5 \cdot 0 \times 2 \cdot 5$ cm. from sheet prepared by high-grade polish Id were coated along the edges and over the upper $3 \cdot 5$ cm. length with a gutta-percha/paraffin-wax mixture. In each experiment the specimen was held vertically from above by a crocodile clip and immersed to a depth of $3 \cdot 0$ cm. in 300 ml. of solution ; the exposed surface of the metal was therefore totally immersed between depths of $1 \cdot 5$ and $3 \cdot 0$ cm. The solution was contained in a cylindrical glass vessel, $9 \cdot 4$ cm. in dia., covered by a filter-paper sheet, and placed inside a draught shield. The temperature was moderately constant, usually between $17°$ and $19°$ C. Potentials were measured against an N/10 calomel electrode, connected only during the period required for measurements ,through a bridge of N/200 sodium chloride. Liquid-junction potentials were neglected, being constant throughout.

TABLE III.
INFLUENCE OF SURFACE FILM ON ELECTRODE POTENTIAL (IN N/200 NaCl).

Specimen Number.	Pre-treatment of Specimen.	Potential (N/10 Calomel Scale). MV. after—				
		1 Min.	1 Hour.	1 Day.	100 Days.*	17 M'ths.*
P14	Polished. High-grade, Id..	+ 16	+ 32	+ 6	+ 28	—
P15	Polished and stripped	− 67	−191	− 97†	+ 10	—
P41	Polished with Al_2O_3.......	−127	−136	− 76	—	+118
P42	Polished with Cr_2O_3.......	− 41	− 41	− 12	—	+146

* End of experiment.　　　　† Period of 2 days.

Typical results are summarised in Table III. Comparing P14 and P15, the stripped surface was markedly less passive than the polished surface, although the difference diminished with time after one hour. The rapid fall in

* Values (expressed in kilogramme-calories) are those given by by M. de Kay Thompson.[9]

potential of the stripped specimen during the first 20 min. is in striking contrast with the slight rise and subsequent steady values of potential recorded for the polished surface. Results from P41 and P42 show the more passive behaviour of steel polished with chromic oxide as compared with that polished with alumina. Although in both cases the surface became more passive with time, the difference between the two persisted for at least 17 months.

REFERENCES.
1 Vernon, Wormwell and Nurse. *Journal of the Chemical Society*, 1939. p. 621.
2 Evans. *Journal of the Chemical Society*, 1927. p. 1020.
3 Hoar and Evans. *Journal of the Chemical Society*, 1932. p. 2476.
4 Evans and Stockdale. *Journal of the Chemical Society*, 1929. p. 2658.
5 Tokumitu. *Nature*, 1940. **145**, p. 589.
6 Miyake. *Scientific Papers of the Institute of Physical and Chemical Research, Japan*, 1937. **31**, Mar., p. 161.
7 Smith. *Journal of the American Chemical Society*, 1936. **58**, p. 173.
8 Erbacher. *Zeitschrift für physikalische Chemie*, 1933. **163**, p. 215.
9 Thompson. " The Total and Free Energies of Formation of the Oxides of Thirty-two Metals," New York, 1942. Electrochemical Society, Inc.
10 Thomas and Price. *Nature*, 1938. **141**, p. 830.
11 Price and Thomas. *Journal of the Institute of Metals*, 1938. **63**, pp. 21 and 29.

Tropical Preservation and Packaging Exhibition

SPONSORED by the Anglo-American Packaging Committee of the Ministry of Production an exhibition of tropical preservation and packaging is being held at the Central Ordnance Depot, Feltham, Middlesex. It is designed to emphasise the importance of adequately protecting stores for the war in the tropics, and to show manufacturers and all concerned with packaging the best means of implementing the new tropical standards in their own works.

That the essential supplies for our Forces be properly packed and proofed must be apparent to all who can appreciate the conditions under which they are battling in the tropics, in the swamps, in the wet and humid forests, and in the South West Pacific's plantations and jungles. According to General MacArthur, actual loss of life results from failure to preserve sufficiently equipment and stores against the devastation of humidity, terrific heat, fungus and all other tropical hazards. The conditions in the Far East are very different from those in Europe. In many countries railways are primitive or non-existent. Roads are few or bad. Terrain varies between rugged mountains, thick jungle, lowlands broken up by narrow valleys, torrential streams or gorges, and flat plains in which river delters and swamps impede progress.

Under such conditions, the packing of equipment and stores to be transported becomes of vital importance. They must be packed to withstand long sea-voyages through the tropics, constant trans-shipment, journeys in lorries and on mules, and storage under bad conditions. In addition, it must be remembered that the difficulties of terrain and the enervating effect of the climate greatly reduces human carrying capacity.

All who are concerned with the packaging of equipment or manufactured goods, whether for the Forces or for normal peace-time export, should make it their business to visit this exhibition, as there is much on view that is of vital importance to the building of a successful exporting business. Although visits to this exhibition are by invitation, this can speedily be arranged without formality by either writing the Commandant, Central Ordnance Depot, Feltham, Middlesex, or telephoning the office at Feltham 2821, Exten. 13.

The Coinage Metals in Antiquity
Part II.—Iran and Irak

By Douglas Rennie Hudson, B.Sc., Ph.D.

(Lecturer in Metallurgy, Heriot-Watt College, Edinburgh).

" . . . la Perse n'a possédé un style qui fûr originairement à elle, mais elle a-très bien su s'emparer du goût assyrien, du goût indien, du goût grec et romain, et donne a ces emprunts un caractère à elle propre. C'est ce qui a constitué son originalité."

DE GOBINEAU.

ABSTRACT.

The author reviews critically the development of process work and craftsmanship in gold, electrum, bronze, and silver in Iran and Irak under the heads—

1. IRANIAN PLATEAU.—Afghanistan (?), *Treasure of the Oxus ;* Persia, *Silver, Gold, The Daric, Tin and lead, Brass and zinc ;* Anau ; Susiana, *Susian metallurgy, Script.*
2. TIGRIS-EUPHRATES BASIN.—Chronology, *Babylon, Ur ;* Early settlement, *Sumerian and Akkadian periods, Babylonia, Assyrian penetration ;* Metal Working in Irak, *Sumerian metallurgy, The bronze-copper anomaly, Bitumen-cored metal artefacts, Babylonian metallurgy, Assyrian metallurgy.*

Horizontally fluted gold rhytons and goblets from the *Treasure of the Oxus* show analogies with the fine vertically fluted goblets from Ur of much earlier date. Much of the late Persian work of chased and inlaid silver plate penetrated into the Kuban, the Don basin, and even into Siberia and China as trade goods. Lead and zinc, extracted from local ores, were used in alloying, centuries before Christ. Susian metallurgy shows Sumerian influence in metal working and Hittite tradition in extraction.

The pre-3000 Sumerian bronze with a constant 10–12% tin was probably synthetised from the metals. Later this vanished, being superseded by copper modified by arsenic, iron, tin, nickel and antimony, the first *Ersatz* alloys. Still later, true bronze of more variable composition reappeared in Irak and also appeared in Egypt. Fine bitumen-cored animal heads from *al Ubaid* near Ur are compared with the Egyptian statues of Pepi, and his son of the sixth dynasty, of copper hammered over a wooden core, with gold head.

4. IRANIAN PLATEAU

GEOGRAPHICALLY, the Iranian massif is a well-defined entity, comprising highly mineralised mountain ranges which rendered communication difficult. Including modern Persia, it stretches from the Elburz range and Southern Turkestan in the north to Baluchistan in the south. In the west it merges through Kurdistan and Armenia into Anatolia, in the east into the high Hindu-Kush mountains. The whole is studded with isolated *tells*, but there is little evidence of important cities radiating a general culture ; the average level was about a millenium behind that of Irak.

Afghanistan (?)

Treasure of the Oxus.—This hoard was discovered in 1877 (?) near a tributary of the Oxus, or at a ford over the river itself on the Samarkand route. It consists of gold jewellery with gem inlays, typical of the *Achæmenian* period, 550–331 B.C., coins, twisted armlets, finely beaten vessels of gold and silver—pitchers and rhytons—of magnificent lines (Fig. 11). Some of the plaques of fashioned gold may actually be modern counterfeits (?) (Fig. 13), whose introduction was rendered easier by the fact that neither origin nor extent of the treasure trove has been satisfactorily settled. Searing comments on the avarice and lack of principle of Rawal Pindi goldsmiths have been made. The vessels show excellent horizontal fluting, reminiscent of the fine vertical fluting of the magnificent gold bowls and goblets of Ur—compare, for example, Figs. 11 and 15. Beasts and animal heads are frequently an integral part of the vessels. Handles are often fashioned in horned and winged animals, very vigorous in concept and finely executed.

For comparison, see the arrogant chamois in silver (Fig. 12) from Armenia, similar objects have been discovered in the Kuban. This specimen, from the Louvre, shows a marked analogy with the art of Sumer, developed much earlier (compare this with Fig. 18).

Persia

Excavation has been carried out chiefly by French and German *savants*, their finds, though not to be compared in splendour with those from neighbouring countries, are nevertheless important. In mural decoration the Iranians excelled. Their low-relief carvings, coloured tiles, and engravings rival the Egyptian in conception and workmanship. Early metal objects are rare, and our knowledge of early Persian history prior to 600 B.C. is, as yet, very imperfect, though after this date it is well authenticated.

Some of the mural work, carried out on a mammoth scale, has survived in the Royal Tombs at Persepolis. Remains, dated by Herzfeld at 3000 B.C., were devoid of metal. In western Persia many bronze artefacts have been unearthed, but great caution is necessary in drawing conclusions. Apart from grave robbery—a thriving industry in the Near East for millenia—importation of occidental metal forgeries is common in Persia.

One of the first finds was the *Treasure of Astrabad*, south-east of the Caspian, discovered before 1844 and comprising gold vessels and copper (but not bronze) weapons.

At Tepe Hissar, south-east of the Elburz range, where three layers have been recognised, gold sheet, silver jewellery and vessels, lead and bronze bowls, and weapons of copper and bronze were recovered. Racket pins

Fig. 11.—Gold ewer from THE TREASURE OF THE OXUS, discovered about 1877 on or near the Oxus, in Afghanistan or Bokhara. Compare the fine horizontal fluting with analogous vertical fluting on Sumerian gold vessels from Ur, about 2,500 years earlier (Fig. 15). Possibly Persian of Achaemenian Period (550-331 B.C.)

attributed to the third millenium B.C. can be correlated with those from Kuban. From Layer II, spear points and double-spiral headed pins of modified coppers resemble Ægean objects, while metal pitchers resemble the Early Minoan.

Silver.—While silver was imported during millenia into Egypt and Irak, Iran possesses widely distributed, though not extensive, deposits of ore. The Arab geographer Abul Feda described mines at Panjire, where the earth, so honeycombed with workings, resembled a sieve. Many early specimens of jewellery and plate—often richly engraved and inlaid—have disintegrated from corrosion by chlorides in the soil, especially when alloyed with copper. Such as remain show highly developed artistic taste and high competence in inlay, chasing and ornament. They have been extensively used as trade goods, being widely distributed along trade routes in Russia and Siberia, as far as Perm ; many examples found their way into the Imperial Hermitage Museum in St. Petersburg.

Gold.—During the fourth and third millenia gold was rare in Iran, but, by contrast, it became very abundant in the first. We may recall the riches of Darius and Xerxes, the splendours of the Imperial Court. Large tributes were exacted from the many conquered nations, silver was acceptable as well as gold—placer, bullion, jewels, all went into the melting-pot. According to Herodotus, re-use of the fabricated articles yielded no difficulty, technical or psychological, to the Persian overlord. What priceless treasures may have been destroyed as a result ! *He melts it down and casts it into*

earthen pots ; when the vessel is full he breaks away the pottery, and when he needs money cuts off as much as serves his purpose.—3, Chap. 96.

Large amounts were also recovered from placers of the Oxus and Dardistan, and their prolificness gave rise to various quaint legends.

The Daric.—Quite apart from his classical imperial fame, Darius is remembered in the name of a gold coin. At first undistinguished, irregular and rough, the *daric* (δαρεικος, Hebrew *darkemon, adarkon*) with its image of a kneeling archer, gradually improved in finish and shape, though it never attained the beauty of the Greek stater (στατήρ) in silver. The emperor was very jealous in maintaining weight and fineness, so that the currency became the accepted standard, not only in the Persian dominions, but in the whole Mediterranean littoral.

Something similar happened with the Spanish-Mexican 8 *real* dollar, the silver *piece of eight*, which passed for centuries literally " from China to Peru " ; it was even countersigned and stamped by the Bank

No. 12.—Chamois in silver forming the handle of a vase in the Louvre. Such a treatment is typical of many metal artefacts of Iranian origin discovered in the Kuban and Armenia. Compare this vigorous and arrogant handling of the winged beast with THE RAM CAUGHT IN A THICKET from Ur, (Fig. 18), more than 2,500 years earlier.

of England (1797–1802), and remains to-day the theoretical basis of the Manchurian dollar (*yuan*). The Maria Theresa *Thaler*, too, remains to-day the actual, and not merely virtual, currency of Ethiopia. Yet neither of these famous standards had a wider circulation than the gold *daric*, if one considers the extent of the then civilised world.

Tin and Lead.—The Greek historian Strabo makes a cursory mention of Persian tin. Exhausted deposits have been found at Seistan and Korossan, but data regarding them are conflicting. If it were safe to regard these as the source of the early tin the author would be prepared to accept this provenance of the tin in the early bronzes of Sumer and Troy. It has been suggested already that these were manufactured in the Lake Van region by the precursors of the Mitanni and Hittites or the Urartu.

Probably more lead objects have been found in Iran than in any other of the ancient countries. Examples are a lead vessel from Tepe Hissar (2000–1600), Anau I (3000 ?), a cube from Elamite Susa. Statuettes, amulets, sheet lead, and even a short length of piping have been reported ! White lead and litharge were probably known to the ancient Persians, and there is little doubt that the products derived from indigenous ore. Lead bronzes are also fairly common amongst ancient metal objects.

Fig. 13. — Plaque from THE TREASURE OF THE OXUS, of hammered thick gold sheet. In view of its divergence from other work in the same hoard, the suggestion has been made that it may be a counterfeit by Rawal Pindi goldsmiths.

Brass and Zinc.—Old deposits of calamine in Irak support the suggestion that white vitriol and zinc oxide were produced before the Christian era as medicaments—e.g., eye-salve—but exact equivalents of archaic words in old manuscripts are uncertain.

Extraction of zinc by distillation in individual crucibles is generally attributed to China, but it may have developed about the same period in Persia. Be

that as it may, some have been bold enough to attribute a Persian root to *spelter*. Strabo's account of *mock silver* is too short to be of much value, but a fair enough description of what the assayer would call the iron-reduction process from a sulphide ore. *There is a stone near Andeira, which when burned becomes iron, and then, when heated in a furnace with a certain kind of earth distills pseudo-silver (ψευδάργυρον) and this with addition of copper makes the alloy as it is called, this is termed mountain copper (ορείχαλκον). It is produced also near Mount T'molos.* ορείχαλκος *was Latinised to orichalchum or aurichalchum.*

Many writers mentioned a golden or yellow-coloured " copper " characteristic of Iran and distinguished from bronze (by its malleability ?) and from gold (by corrodibility and perhaps density ?). When annealed and polished, brass and gold must have appeared very similar in appearance, lustre and working properties, to the ancient metallurgists, especially when they dealt with gold alloys.

Anau

At Anau in South Turkestan three layers were identified by Schmidt, and provisionally dated 3000, 2000 and 1000 B.C., a decision which has since been questioned. Some bitter debate has occurred amongst archæologists whether pottery from Anau I can be correlated with Susa. In this layer arsenical and antimonial coppers were found, as well as lead. Gold, silver and bronze were absent from I and II, variable tin bronzes and leaded bronze were found in Anau III. The late occur-

Fig. 14.—Weight, with handle, from Susa, in the form of a conventional lion in bronze. Note the exquisite pattern-making and the technical perfection of the casting. Many other examples exist in the same style, some with inscriptions in Aramaic, Assyrian, Akkadian.

rence of the metals is remarkable, particularly in view of the nearness of rich sources. Pottery vessels from II and III may be equated with similar products, from Anatolia and from Egypt, respectively. A ferrous culture of Persian age has been termed Anau IV.

Susiana

Of all Iranian relics, those of Susa, the chief city of Elem, are best known to the layman. Excavation in this

Fig. 15.—Tumbler and bowl in gold with fine vertical fluting, from QUEEN SHUB-AD'S GRAVE. Approximately half scale.

area, about 150 miles north-east of Ur, has been relatively detailed. Finds from the two cities are often considered together, though strictly the cultures are different. However, trade and political connections were always very close, and the magnificent Sumerian civilisation left its mark upon Susa, particularly in the earliest layers. Political rivalry was intense, but neither city was able to maintain military ascendance and the overlordship changed frequently.

Susian Metallurgy.—Susa I is attributed to the chalcolithic age—i.e., the transition period in which copper and stone were in use simultaneously. In Egypt, as has been shown, this extended over many centuries. 3000–2800 B.C. has been suggested for Susa I, and there is a close correlation between Susa IA pottery and that of al Ubaid.

Archæologists suggest a lacuna between this layer and II, dated at 2750–2500, the Elamite or Japhetic culture showing evidence (from pottery) of contact with the Punjab.

Bronze has been recovered in quantity, dating from the third millenium onwards, including weapons, axes, tools, ornaments. Much of the work is of high artistic attainment (Fig. 14). It shows great skill in alloying and manipulation, and possibly even multiple casting.

Tooling of statuettes with gold sheet similar to Assyrian technique was carried out as early as 2500 B.C. In the author's view, both can be attributed to the same accomplished pre-Hittite tradition.

In general, the alloys were rather higher in tin than the standard 10–12% typical of Irak, and would therefore be more easily cast. It is likely that some objects reported as bronze in the nineteenth century without chemical examination are really copper, but there is no trustworthy evidence of the use of bronze prior to copper as in Ur.

Statuettes and ornaments of gold and silver have been dated at eleventh century B.C. rather uncertainly. Ingots of these metals with cuneiform inscriptions have been found—this is probably of little chronological significance since old characters have always maintained a peculiar intrinsic value in religious and ceremonial inscriptions. Together with electrum and bronze, these metals were used lavishly in palace decoration.

Script.—The ancient Elemite script possesses some characters cognate with the same Sumerian characters, but more primitive.

5. TIGRIS—EUPHRATES BASIN
Chronology

Babylon.—In the recorded chronology, which is probably authentic from about 2000, the date assigned

Fig. 17.—Ceremonial dagger with gold blade and granular decoration, and dagger with gold-plated handle. Approximately one third actual size.

to the first dynasty, a clerical slip of 1000 in the cuneiform has been detected, but this is very different from Berossos' reckless inexactitudes. The year 763 B.C. is fixed by a recorded eclipse. A flourishing civilisation existed in Babylon in the fifth millennium B.C.

Ur.—The record of the scribe Berossos, giving the fantastic date of 20,000 B.C. for the first dynasty at Ur, is now regarded as nothing better than religious manipulation. From the Sumerian Royal Canon, compiled about 2000, a date of 4600 is obtained. Since this is known only by reconstruction from fragments scattered in various Babylonian archives, there is ample room for error, even if the statements in it are trustworthy—this is probably the case. The first dynasty is now advanced to a date variously given between 3100 and 2950. Subject to vigorous *ad hoc* warning of the fallibility of correlating time with depth of deposit in the 18 layers extending through 60 feet, CHILDE has estimated 4500 for Erech and 5000 " as a moderate date " for Tel Halaf. Probably Samarra is still older. " Ur of the Chaldees " is of interest as the home of the Prophet Abraham of the Pentateuch, Talmud and Koran.

Early Settlement

Sumerian and Akkadian Periods.—So far as one can deduce, the original Semitic inhabitants were displaced by non-Semitic Sumerians, penetrating from Central Asia along the Caspian Sea, with cultural attainment already high. Their mythology shows evidence of evolution *in situ ;* the flood of Genesis is preserved in their tradition as an historical fact and confirmed in archæological excavation. They had an organised military structure, wore woollen fabric, excelled in brick (though not stone) construction, made accurate records on clay tablets in wedge (Lat. *cuneus*) script. Subsequently, there was an invasion by Semites, who settled

Fig. 16.—Helmet of MES-KALUM-DUG in gold, approximately half scale. Actual height 23 cm.

in Agade, and the races partitioned the land. Eventually the Akkadians under King Sargon, 2630 (?) obtained supremacy, and their language displaced Sumerian, though the wedge character proved very persistent. It was adopted by the Lake Van peoples and even by Persia, and continued in use by the Phœnicians until they adopted a modification of the Egyptian script. With the sack of Ur by Elamites about 2170, its importance as an individual city ceased, with the dissociation of Sumer into independent city states ruled by knights. *Invention of writing is generally credited to Sumerians*, but the Egyptians came very near. Early Sumerian culture was not homogeneous, and there is evidence of a sudden impetus, perhaps due to infusion of new blood, these invaders may even have introduced the cuneiform. The proto-Sumerians were quite familiar with metal working, and very competent ; not only gold, but copper, and *electrum* containing one-fourth of silver, have been recovered. See Figs. 15, 16, 17, 18 for magnificent examples.

Babylonia.—Greek Βαβυλωνία and Hebrew BABEL from *Babili*, " The Gate of God." Invaders, probably Semitic Amorites, entered Babylon, wrested the control and set up a local dynasty. About 1950 the great lawgiver Chammurabi successfully unified the mosaic of

Bitumen core
of lion's head.

Bull.   Stag.   Panther.

Fig. 19.—The remarkable Sumerian technique of bitumen cores on shells of copper and gold, circa 3000 B.C. The illustration shows fine specimens of heads of the bull, stag, and panther, and the bitumen core of a life-sized lion's head, with tongue, teeth, and eyes of jaspar, shell, and schist, and fragments of the copper.

peoples in the first dynasty. About 1926 B.C. Hittites from the Cappadocian highlands captured and looted the city, but they in turn were too weak to withstand the Kassites in 1750, and Sumer too far away to render assistance. Little is known of these warlike mountain tribes, probably ancestors of the Kurds, although their (third, Kassite) dynasty lasted six centuries. On his visit to Babylon, Herodotus was greatly impressed by its magnificence, and his descriptions have been substantially confirmed on excavation.

Assyrian Penetration.—Assyrians gradually spread down from their capital at Ashur in the north between 2700 and 2000. Their culture was Subaraean, and in standing conflict with the Sumerian. Superb in military training and equipment, they even used a rudimentary tank, with the observation officer protected by plating, but despite these martial accomplishments, they remained at a low level culturally. Of all Assyrian kings, the brutal and capable Sennacherib is best known. Victorious everywhere, he marched his army to an Egyptian frontier post at Pelusium where plague (?) *smote in the camp of the Assyrians an hundred four score and five thousand ; and when they arose early in the morning, behold, they were all dead corpses. So Sennacherib king of Assyria departed, and went and returned and dwelt at Nineveh.*—Kings 2, 29. The disaster is confirmed historically. However, he continued successful, defeated the Greeks, captured Tarsus, and destroyed Babylon in 698 B.C.

By 1250 B.C. the expanding Assyrian power had secured domain over " The Land of Sumer and Akkad." An official history " published by authority " on clay tablets still survives in the British Museum. By 1400 B.C. Assyrian had become the diplomatic language of the then civilised world, and an extensive correspondence with Egypt is still extant. About the eighth century B.C. this was superseded by Syriac, or Aramaic Hebrew, in

which the Gemara Talmud and the Chaldee Paraphrase of the Old Testament were written. This is probably the tongue which Christ Himself spoke.

In 606 B.C. Nineveh was overthrown by a mixed force of Medes and Babylonians ; the " New Babylonian Empire " lasted from 625 to 538 B.C., when it was incorporated in the relatively benevolent Persian hegemony. In 331 B.C. Emperor Darius (not " the Great ") was overcome by Alexander during the historic campaign in which he conquered Persia. With the fall of the Assyrians, culture rapidly declined in Irak and the old level was never recovered.

Metal Working in Irak

Sumerian Metallurgy.—The Sumerians were excellent craftsmen in metal. Predynastic levels in Kish and Ur, 3500 B.C. or perhaps earlier, show very high attainment in design and execution (Figs. 15, 16, 17, 18 show high craftsmanship). Design, however, became stylised ; after the first dynasty degradation was relatively rapid, although the standard never fell very low. Simultaneous with this artistic decline a change in metallurgical technique is apparent. Earliest bronzes at Ur cemetery have a tin content of 12% and are essentially *castings*. In later specimens the composition is variable with tin gradually diminishing to almost zero by about 3000 B.C., while a fraction of 1% nickel is present, and sometimes arsenic as well. This *modified copper* was almost always cold-worked by hammering. This is in good accord with the metallurgical characteristics ; the castable bronze with liquidus about 860° and solidus 790° being much harder intrinsically than the copper with higher melting-point at 1,084° C.

The Bronze-Copper Anomaly.—Frankly, one is puzzled as to the conclusion to be drawn from Ur bronzes, though voluminous data are available. Excavation in Irak is about a quarter-century behind that of Egypt, and present-day digging is carried out with the utmost care. The salient points are—

1. The consistent composition of pre-dynastic bronzes is good evidence for alloying by synthesis pre-3500 B.C.

2. The remarkably constant 0·3% nickel in the artefacts of modified copper about 3000 B.C. is good evidence for a nickeliferous copper ore, rather than for alloying by synthesis or addition of a nickel ore, to the copper smelting charge.

3. It is attractive to correlate the obvious decline from the pre-dynastic summit of taste and craftsmanship with a conjectured contemporary decline in alloying skill, but of this the author is not convinced.

The view in (2) is opposed to the classical archæological scheme of a " bronze age " following the " copper age." Yet these " ages " are like geological strata, they vary in depth (time) at different ages, and may peter out altogether. The Sudan passed directly from neolithic to iron culture, while the Australian blackfellow is hardly emerged from the stone age.

It is hardly conceivable that a tin content could be maintained so consistently at 10–12% by smelting mixed

Fig. 20.—Statue of King Pepi I followed by his son, Prince Montesuphis, VI dynasty, circa 2000 B.C. The trunk and limbs are of copper sheet hammered over a wooden core, and riveted ; feet and hands are probably cire-perdu castings. The head a gold casting, shows astonishing vigour. Compare this life-sized statue with the bitumen-cored copper shells at al 'Ubaid (Fig. 19). The above Egyptian statue is about half a millenium later than the Sumerian work.

Fig. 21.—Bronze band from the gates of Shalmaneser III, king of Assyria 859-824 B.C. The upper portion shows the king seated with archers on the right and military engineers (?) on the left. The lower panel shows an attack with the battering ram.

ores, especially with the primitive furnaces then available.

In the case of Troy, one of the first sites to be excavated by the industrious and successful SCHLIEMANN, a similar anomaly has caused much heart-searching. Bronze with 5-3% tin is common in Layer II, as is silver and gold in jewellery and ingots, but copper (modified) is rare in Layer I, and the tin content of the bronze in IV is less and variable. In view of the haphazard, if not nonchalant, methods of digging before technique had developed, some distinguished workers have tacitly assumed a confusion either of specimens or layers. But this facile explanation (which may yet be correct) will definitely not hold for Ur specimens, of which, moreover, chemical analysis has been both careful and detailed.

In view of the copper-bronze-copper sequence in both Irak and Hissarlik, one is disposed to accept it as factual, subject always to errors in composition, and especially in visual identification, of the Trojan objects. We may conveniently leave an " explanation " to the prehistorians. In the author's view, already expressed in the discussion on Egyptian bronze, the anomaly is due to a drying up of the bronze supply, from exhaustion of the tin deposits. This implies that the ferrous, nickeliferous and arsenical coppers are the earliest examples of Ersatz alloys. Later, bronze was probably synthetised from tin imported from Spain or Cornwall by the Phœnicians.

Much useful information on compositions has been collated by the British Association Committee on Sumerian Copper, under chairmanship of Peake and subsequently of Desch. With more general recognition of the value of micro-chemical analysis, it may be hoped that many collectors and curators will be willing to sacrifice a few inconspicuous drillings.

Bitumen-cored Metal Artefacts.—Fig. 19 shows some excellent examples of the peculiar bitumen-cored metal shells characteristic of Sumer. This magnificent find by HALL came from a pit or *cache* below a more recent pavement at Al Ubaid, about 4 miles west of Ur, and is dated at 3000 B.C. This is perhaps conservative, as one would expect from the British Museum. A bitumen core for a lion's head, with tongue, teeth and eyes of jaspar, shell and schist, is shown ; there are also finely executed copper heads of a bull, stag and panther. The larger statues are partly cast and partly hammered metal, or so it has been reported. How regrettable that any doubt should remain on a subject which a competent metallographer could clear up so directly and conclusively with so little sacrifice of metal !

A cold-worked microstructure would establish either casting of the molten bitumen into a cold-worked shell, or hammering of the sheet on a pre-fashioned armature. Microscopical and physical examination together should suffice to differentiate between these possibilities. Dendritic structure in the metal would indicate a cast bitumen core. Similar technique seems to have been used in the vigorous Egyptian statue of Pepi I and his son, of copper sheets hammered over a wooden core. Here, as in the introduction of bronze, Egyptian practice (2400 B.C.) is many centuries later than Sumerian. (Fig. 20.)

Babylonian Metallurgy.—The Babylonians seem to have been particularly skilled in alloying. Thus, one cannot deduce safely the gold content of an object from its colour, as in Egypt. An alloy with 60% silver and 10% copper was more " golden " than many specimens of native gold. They also " coloured " gold like the Victorian jeweller—an artificially rich skin was produced by acid treatment followed by burnishing. Different " golds " were recognised—red or ruddy, white or glowing, fine, pure, refined, poor ; the first and second may have been alloys with copper and with silver,

Fig. 18.—" THE RAM CAUGHT IN A THICKET," in gold, approximately one third actual size. Actual height 50 cm.

or lacquers may have been used. Since rough quantitative fire assaying was in use at 1500 B.C., it is a fair conclusion that these varieties were intentionally synthetised rather than adventitious or native alloys. One of King Chammurabi's circular clay tablets authorises a steward to cut down *abba* trunks of good quality, in definite lengths, for metal smelting.

Assyrian Metallurgy.—In their gift for mercantilism, exchange, and barter, the Assyrians remind us of the Phœnicians much later. They sent trade goods by commercial missions to neighbouring countries, and in these metal artefacts were prominent. In ore extraction they were highly skilled, due probably to Hittite influence. Their military success, too, has been attributed to imported Hittite iron weapons, at this time daggers were often included in tribute.

King Sennacherib (705–681 B.C.) boasted of casting enormous temple gates in bronze " as though they had been *shekels* or half *shekels*." That no trace of these remains, will surprise nobody, yet not even a tradition lingers. Pillars from Solomon's temple were reported to be standing in·*Porta Latina* in Rome in the twelfth century A.D., despite the statement that they had been broken up and carried away by the Chaldees. Too much credence need not be placed in the mediæval report, since they were said to sweat water on each anniversary of Jerusalem's destruction, but the important point is that the tradition was alive. With Sennacherib's great castings—beasts of 11,000 *talents*, pillars of 6,000 *talents*— it is completely wanting. They may yet be unearthed in Mesopotamia, but the masses are extremely large, since 1 *talent* = 0·6 cwt. approx. Perhaps we should assume a clerical error similar to that in Babylonian chronology.

Fig. 21 shows a fine Assyrian cast bronze in the British Museum from a set of 13 ornamenting the gates of Shalmaneser III, who reigned about one and a half centuries before Sennacherib. There is also a much-worn bronze threshold of Nebuchadnezzar II of the New Babylonian Empire, 604–561, while Assyrian tradition was still very strong.

Even before this, purification of silver (by cupellation ?) was understood. A thoroughly modern system of hall-marking had been established with different proof marks for the assay offices in various towns.

Diamond Tool Research

DIAMOND tools are employed in numerous industries·but, in engineering, diamonds are used for the most important engine components, such as pistons and crankshaft bearings, commutators and printing rollers, besides their application for truing precision grinding wheels and in hardness testing. For those dealing with these tools in production, it may be of interest to know that an independent research department has recently been established by the Diamond Trading Co., Ltd., the main importers of industrial diamonds, and besides its scientific research activities, this department is in a position to test individual tools and to submit reports on them. The following equipment is at present at its disposal : High- and low-power microscopes with polarised and monochromatic light with photo-micro equipment, high-power projector, optical goniometer, optical equipment for measuring the radii of spherical surfaces. X-ray investigations are made in collaboration with other Institutes. Work recently carried out includes abrasion test on truing diamonds, investigations into the crystal orientation of shaped diamond tools by X-ray crystallography, the testing of settings of industrial diamonds by means of X-rays, the testing of abrasive powders by X-ray diffraction methods, the testing of the surface finish of diamond surfaces and surfaces machined with diamond. The services of the department are free to industry, and inquiries are welcomed. The address is 32-34, Holborn Viaduct, London, E.C. 1. Visits by appointment.

Hydraulically Pressed Light Alloy Pistons

By Cecil Kimber

(*Works Director, Specialloid, Ltd.*)

Developments in the application and processing of light alloys for pistons are discussed. The increasing need for greater strength for a given weight, under arduous operating conditions, gradually led to the use of forged light metal pistons instead of the cast type. Two methods of producing wrought pistons are considered—hammered and pressed forgings— and particular attention is directed to the latter method for which the blanks are prepared by extrusion. Brief reference is made to the plant and equipment used in works especially designed for the production of light alloy pistons by the pressed method.

RATHER less than twenty-five years ago the aluminium piston began to be generally used as a result of the search for greater engine efficiency. Progress was principally in the design and metallurgical fields, and the process of manufacture was by casting. Gradually, the technique of casting improved from simple sand castings to semi-chill and die castings ; during this time it was found necessary to exercise stricter control of casting temperatures, and much research was carried out into the chemical and physical properties of the various alloys that came into use.

Then in the early 1930's aircraft engine designers began to realise the necessity for pistons having not only the combined properties of high thermal conductivity and good heat dissipation, but good recovery value ; the material from which they were made was required to withstand repeated heating and cooling without having a marked detrimental effect on its properties. A cast piston has this good recovery value, but lacks the tensile strength of the pressed or forged piston and also is apt to suffer from variations in soundness. In service aero engine pistons operate at exceedingly high temperatures, sometimes exceeding 400° C., but these temperatures are not uniform over the whole body of the piston. These steep temperature gradients mean that the material used should have good structural and dimensional stability. Structural to ensure strength at elevated operating temperature and dimensional stability to avoid distortion in service. There must also be good resistance to wear and also good machinability. Not only in aircraft engines but in compression ignition engines pistons are required with widely varying properties. Being a reciprocating part the weight has, in aero pistons, to be as low as possible commensurate with the thermal capacity. As these limits are narrow it is vitally essential that the whole technique of manufacture from the preparation of the virgin metal to the fabrication of the piston is such that will give uniformity of results.

Continuous research and development of the light aluminium and magnesium alloys by both metallurgists and designers and the co-operation of the actual pro-
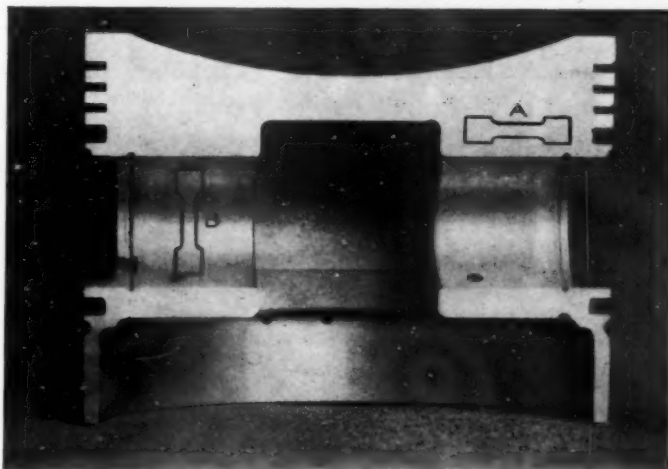

Fig. 1.—Sectioned aero engine piston marked where the two test-pieces are cut, one in the axial direction and the other at right angles to the axis.

ducers of pistons have largely overcome the difficulties involved in their production and enabled achievement of the present high standard. Indeed it is probable that during recent years there have been greater advances in this field than in any other branch of metallurgy.

In spite of the fact that over the years mentioned, foundry technique has improved and is so closely controlled that the piston manufacturer can maintain a very high level of quality in cast pistons, the need for greater strength for a given weight, under arduous operating conditions, inevitably forced the use of wrought material. The aircraft industry was the first to recognise the need and to use wrought alloys in the manufacture of pistons, but with the big advances that have been and are being made in high output compression ignition engines, it is inevitable that the Diesel engine field will also look in the same direction. Broadly speaking, there are two methods of producing wrought piston blanks. Common to both methods is the production of cast ingots. It can be a simple form of die-casting, but production requires particular care and attention if sound blanks are to be obtained from them. This is of
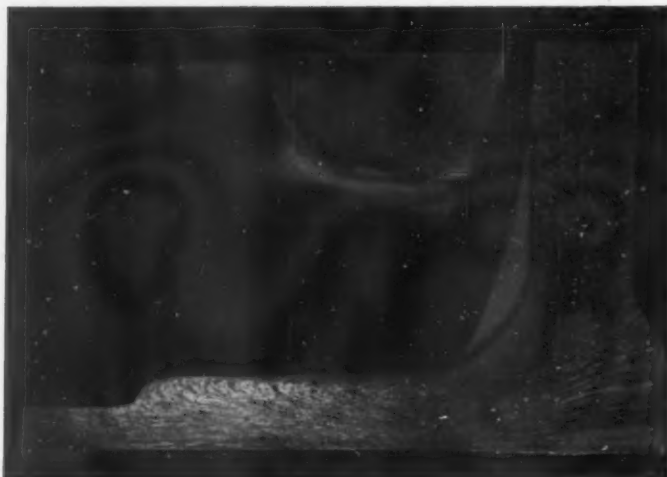
Fig. 2.—Illustration showing the grain flow of a pressed piston which contributes so much to its good tensile properties.

ingots in their moulds. It is incorrect to imagine that porous areas in the ingot will be eliminated by the welding together of the material during the forging (or extruding) operation. This is not the case, and such defects will cause laminations. It is for this reason special technique is necessary in the casting of these ingots.

The common practice is to use water-cooled iron cannon moulds, but there is an alternative technique which involves casting the ingots in canisters made from $\frac{1}{8}$ in. sheet steel. These cylindrical cans are contained in an outer jacket which, after the completion of the pouring, can be filled with cold water, giving a rapid rate of chilling. Other and more modern methods of casting are the various continuous casting processes, each one having facilities for the rapid cooling of the ingot.

special importance because the majority of the reject pistons encountered are due to faulty ingot material.
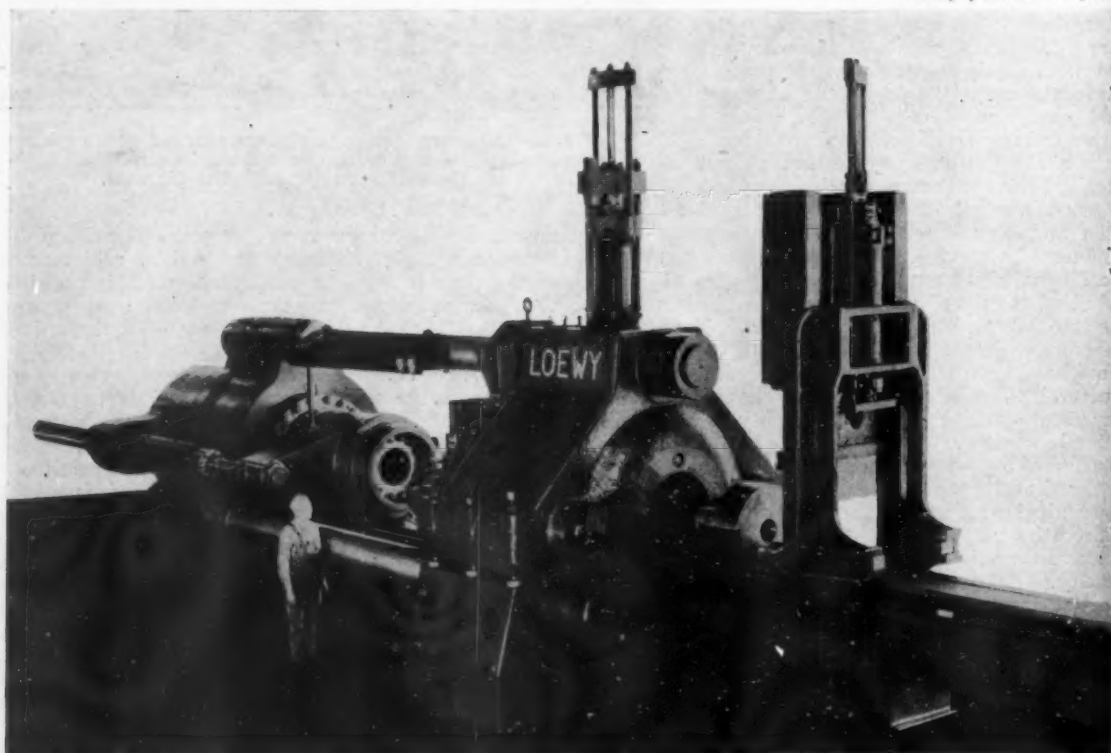
Cast Ingots

The ingot must be sound and free from porosity and contraction cracks ; it should have a fine equiaxed structure, excluding the coarse columnar structure which tends to form during the cooling of such

Drop-forged Pistons

The current practice in this country and, until recently, in America, is to produce the finished aero engine piston from a blank worked by the "dummied" or hammering and stamping method. In the case of this forged component, the ingot is first turned and cut off into suitable billets providing sufficient material for making the solid blank form which the piston will be manufactured. These cylindrical blanks are then heated in an electrical muffle furnace or a nitrate salt bath for a suitable period to provide complete soaking.

Fig. 3.—The type of press, with a capacity ranging up to 5,000 tons, used for extruding light alloy bars for hydro pressed pistons.

Courtesy of Automobile Engineer.

Then, in order thoroughly to break down the cast structure, these blanks are put under a drop hammer and, in order to obtain the most suitable grain flow throughout, the sections of the finished piston are "dummied" into a series of various shapes and finally fitted into a die for the drop-stamping operation. The "dummying" operations and the final stamping tends to create a partial directional flow of the grain, but, to some extent, the advantages derived from this formation are frequently lost during the machining, with the result that the final product is left with parallel lines of grain flow transverse to the section of the piston. For example, if a typical forged piston is studied in order to determine the effect on tensile strength of this grain flow, it is not uncommon to find a variation of as much as 3 tons loss in tensile strength in the axial direction, as against the maximum figures at right angles to the axis.

The following figures have been compiled from actual tests from a range of pistons, whilst Fig. 1 shows the positions from which the axial and 90° to axial test-pieces were taken from the piston.

TESTS ON FORGED PISTONS.

Type: Rolls-Royce Merlin. Alloy: L 42. Process: Forged. Analysis, % 9—Cu, 1·75; Fe, 1·13; Ni, 0·78; Si, 1·07; Mg, 1·59; Other Ti, 0·05.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	26·5	3·0	5·5
90° to axial	23·5	3·0	1·5

Type: Rolls-Royce Kestrel. Alloy, L 43. Process: Forged. Analysis, %:—Cu, 4·15; Fe, 0·37; Ni, 2·02; Si, 0·33; Mg, 1·67. Other—

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	26·5	3·0	5·5
90° to axial	23·5	3·0	1·5

Type: Bristol Mercury. Alloy: L 42. Process: Forged. Analysis %:—Cu, 2·05; Fe, 1·32; Ni, 1·24; Si, 0·89; Mg, 1·64; Other Ti, 0·07.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	27·5	8·0	9·0
90° to axial	25·5	3·0	2·0

Type: Bristol "Hercules" II. Alloy: L 42. Process: Forged. Analysis, %:—Cu, 2·05; Fe, 1·17; Ni, 1·18; Si, 1·0; Mg, 1·65; Ti, 0·05.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	20·75	13	12
90° to axial	14·5	2	2

TESTS ON PRESSED PISTONS.

Type: Armstrong Siddely Deerhound. Alloy: 2L42. Process: Pressed. Analysis, %: Cu, 2·25; Ni, 1·30; Mg, 1·50; Fe, 1·10; Si, 1·00; Ti, 0·10.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	26·20	15·0	114
90° to axial	26·00	13·0	114
Irregular grain flow	25·60	9·0	114

Type: Pratt and Whitney Wasp. Alloy: Similar to LO-Ex. Process: Pressed. Analysis, %: Cu, 0·75; Ni, 1·48; Fe, 0·43; Si, 9·92.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	21·0	4·0	9·0
90° to axial	20·75	2·0	2·5
Irregular grain flow	18·0	5·0	9·0

Type: Wright Cyclone. Alloy: L 43. Process: Pressed. Analysis, %: Cu, 3·0; Ni, 1·93; Mg, 0·89; Fe, 0·47; Si, 0·61; Others, Nil.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	R.O.A., %.
Axial direction	25·25	8·0	12·0
90° to axial	25·50	10·0	11·0
Irregular grain flow	17·75	14·0	15·0

Type: B.M.W. Aero. Alloy: Similar to LO-EX. Process: Pressed. Analysis, %: Cu, 0·55; Ni, 0·76; Mg, 0·90; Fe, 0·36; Si, 11·50; Ti, 0·05; Mn, Nil; Zn, Nil.

Tensile Tests.	Max. Stress, Tons/Sq. In.	Elongation, %.	B.H.N., %.
Axial direction	14·50	5·0	119
90° to axial	14·25	5·0	—
Irregular grain flow	12·50	4·0	—

The major objection to the production of pistons made from forged blanks is the human element; reliance must

Fig. 4.—1,000-ton hydraulic presses installed at the works of Specialloid, Ltd., for pistons. The water-prefilling tanks are on the left of each press.
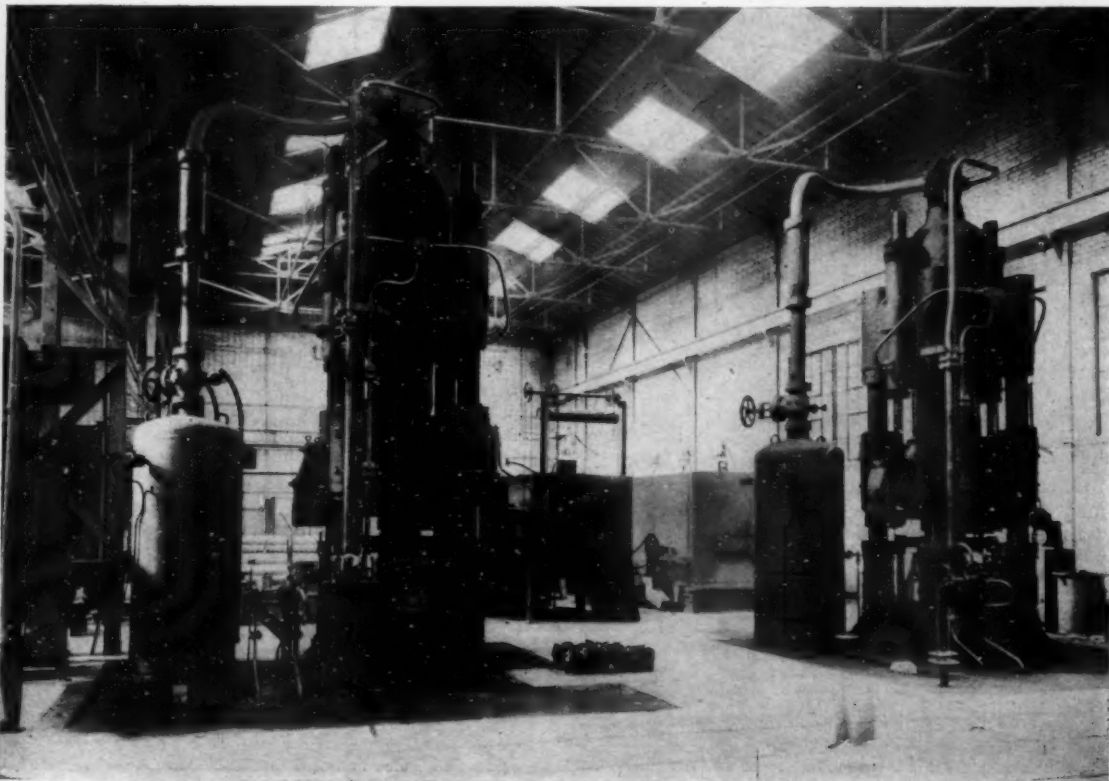
Fig. 5.—Crosshead and tool holder on the Loewy presses.

Courtesy of Automobile Engineer.

the pressed piston has definite advantages over the drop-forged piston. The important point to remember is that the forging of aluminium is an operation of repeatedly deforming a bar or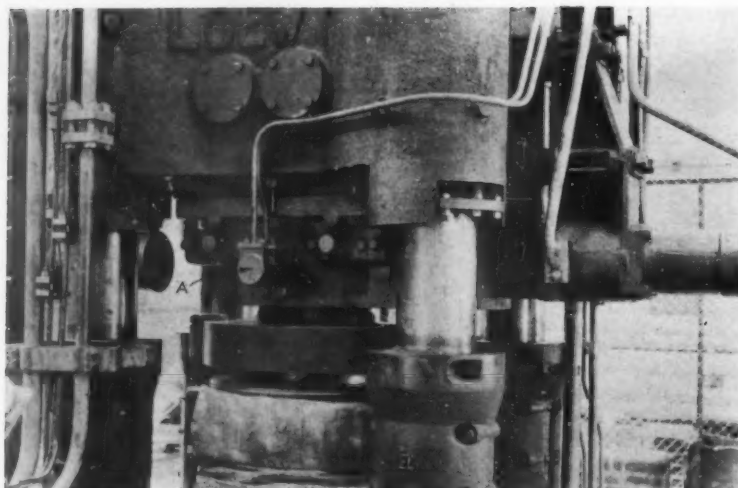 blank above the recrystallisation temperature and within the soft range of the metal by hammering or pressing to shape near to that of the finished product.

When forged aluminium alloys are used for highly stressed components, such as aircraft or compression-ignition engine pistons, the importance of grain flow is of a very high order. In press-forging the plastic deformation is affected by the means of relatively slow squeezing process that ensures the gradual and uniform distribution of the plastic deformation over a much greater area than the much more severe and localised deformation which is imparted by the drop-hammer method. (See Fig. 2.)

be placed upon the skill of the operator in carrying out the " dummying " operations and the inability to ensure uniform results, particularly between one operator and another. These hammer blows have to be gauged accurately and must fall in a correct position on the blank in order to break down the cast structure uniformly. This would appear to be most difficult to achieve, judging from a number of examinations made on forged pistons, as variations in grain size were apparent. Such variations in grain size are apt to cause differences in the mechanical properties and, from a loading point of view in service, to affect the distribution of stress. Even so, the production of pistons by this forging process showed great advantages over even the best that could be produced by any form of casting. However, our engineers felt that this was not the complete answer, especially as experience in other countries appeared to show that more advanced methods of production gave better technical results.

Pressed Piston

These later developments concerned the use of pressed forgings as opposed to hammered forgings. Experience has shown that the resultant working is much more accurate than that produced by the hammer process, and consequently a pressed piston can be produced to much closer limits than the drop-forged piston. In addition, the amount of draft required on the tools is much less, the pressed piston needing only 1° of included angle draft, whereas that for the drop-forging needs from 7° to 10°. Further, there is a greater economy in material, and in wartime any saving in virgin metal is of vital importance, whilst in the post-war economic world a similar saving is also important. Owing to the greater accuracy of the press operation, the finished piston blank is much nearer the shape of the final product and thus machining technique is greatly simplified and the amount of metal to be removed is much less. As an example, the weight before the machining of a pressed piston is approximately only 65% of the weight of the drop-forged piston of the same type.

Exhaustive investigations and tests have proved that

Another great advantage of the press method of piston fabrication is that once working conditions have been established they remain uniform and the amount and rate of work on the blank are governed entirely by the tool design and the speed of the stroke ; that is solely by machine factors. They can therefore be repeated

Fig. 6.—Wild-Barfield 30 kw. furnace used for heating piston blanks to forging temperature.

Courtesy of Automobile Engineer.
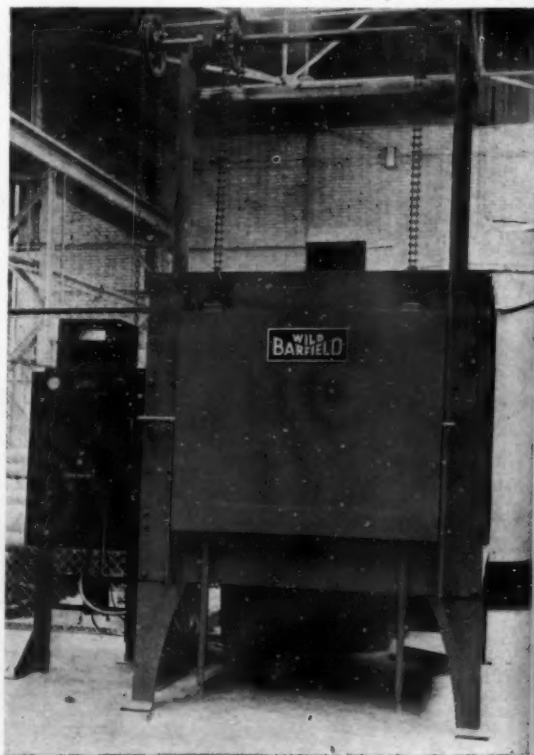
exactly again and again independent
of the operator. Our engineers have
exhaustively studied the whole
question of forged piston production
and have come to the conclusion
that the best way to achieve this
was :—

(1) To use extruded section made
    from billets cast by one of the
    known continuous casting pro-
    cesses whereby much greater
    uniformity of results could be
    depended upon than by the
    previous methods, and

(2) Hydraulically pressing the
    piston from machined blanks
    cut off such extruded bar. By
    doing this they were convinced
    that much greater uniformity
    of results independent of the
    operator could be achieved and

    (a) useful economies in
        material would be obtained.

    (b) Much better grain flow re-
        sulting in

    (c) Better tensile results over
        the principal sections of the
        piston.

Regarding the question of stock above a certain
diameter, when the blanks required are too big to be
extruded, the cast stock has to be " dummied " under
the hammer before being pressed, and in order to cope
with contingencies of this nature, drop-hammer capacity
is included in the plant laid down at our works.

In dealing with the question of extrusion, one of the
main advantages is that the rate of extrusion can be
controlled, maintained and reproduced at will, and
having therefore established conditions of temperature
and speed of operation, together with other factors
concerning the reduction of diameter, repetition of
extruded stock having the same characteristics can be
relied upon.

Extrusion is of course the forcing of metal heated to a
plastic state through dies by the application of adequate
high pressure, and presses of 5,000 tons are capable of

Courtesy of Automobile Engineer.

Fig. 8.—A corner of the physical laboratory.

producing extruded stock up to 7 in. in diameter. Fig. 3
shows an extrusion press in operation. Aluminium and
magnesium alloys have relatively low critical tempera-
tures, and at the still lower temperatures which must be
used for extrusion, they are not very plastic. The speeds
employed for extruding are much lower than those used
in the extrusion of steel, and are, of course, governed
by the amount of work done in reducing the ingot to the
desired size and the composition of the alloy. In practice,
speeds varying from 2 ft. to 6 ft. per min. are employed.
The flow of the metal, when using the direct method of
extrusion, is interesting as only that directly opposite
the die aperture—that is, the central portion of the ingot
—flows forward, the remainder of the metal, adjacent
to the die face, cannot flow forward neither can the ingot
expand diametrically, because it is confined by the
container. It therefore follows that the metal must
flow backwards and then down the centre ; in effect, the
ingot is forced completely inside out. This is one of the
advantages peculiar to the extrusion process, because
it means that any internal faults in the original ingot
are exposed on the surface of the extruded bar and at
the same time the complete " working " of the stock
is ensured.

Equipment

There are three types of presses available for manu-
facturing pressed pistons. The eccentric crank pattern,
the friction screw type, and that which is hydraulically
actuated. The two former entail less capital outlay and
are of simplest construction in so far as they are self-
contained. However, our engineers came to the con-
clusion that, in spite of the increased capital outlay,
hydraulic presses have such greater sensitivity of control
which is an important factor in the production of high
quality pressings, that it was decided to install this
type. (See Fig. 4.)

Working pressures and pressing speeds are more easily
and accurately controlled on presses that are

**Fig. 7.—The discharge end of the G.E.C. electric
conveyer furnace.**

Courtesy of Automobile Engineer.

Fig. 9.—The heat-treatment section.

hydraulically actuated, particularly in fabricating aluminium and magnesium alloys which are not so easily worked as steel. Also it must be remembered

that the resistance offered to deformation by the aluminium alloys is approximately twice that offered by soft steel, and one and a half times that of nickel chrome steel. Large capacity presses were therefore necessary, and those installed at our works are of 1,000-ton capacity. They were designed and built to the company's specification by the Loewy Engineering Co., Ltd., and include all the refinements that experience has shown to be necessary for producing the pressed type piston. The pressure water plant for feeding the presses consists of a pistonless air hydraulic accumulator, a three-stage air compressor which charges the air bottles at a pressure of 4,250 lb. per sq. in.

As will be seen from Fig. 4, each of the presses are of the four-column vertical type, and as one of the main advantages which must be associated with the pressed piston is the elimination of unnecessary machining, it is necessary to have accurate and repeated reproduction of the internal form. Only absolute rigidity and exact alignment of the tools can achieve this, and these features were given special consideration in the design of the presses.

One special feature incorporated into these presses is the provision made for lateral movement of the tool-holder in respect to the cross-head for use where certain forms of pistons cannot be produced in a single operation, but require two-stage pressings. By this adaptability the presses installed can effect considerable production economies as compared with the ordinary single-punch press, where it would be necessary to do the first stage pressing on a batch of blanks, change the punch, reheat the partly finished pistons to the correct working temperature again, and then complete the second press operation.

With two-stage pressing, two punches are mounted in

Fig. 10.—The chemical laboratory which has been specially equipped for rapid and accurate analyses of light alloys.

Courtesy of Automobile Engineer.

the tool-holder, one for the first stage and the other for the second stage. When the first stage punch is fully retracted the tool-holder is hydraulically moved laterally to bring the second punch into line with the die. The sequence of the approach stroke and the pressure stroke is then carried out for this second stage. By this means only one heating of the piston blank and one loading and unloading operation is required, reducing as well as simplifying the work. This method of construction is shown in Fig. 5.
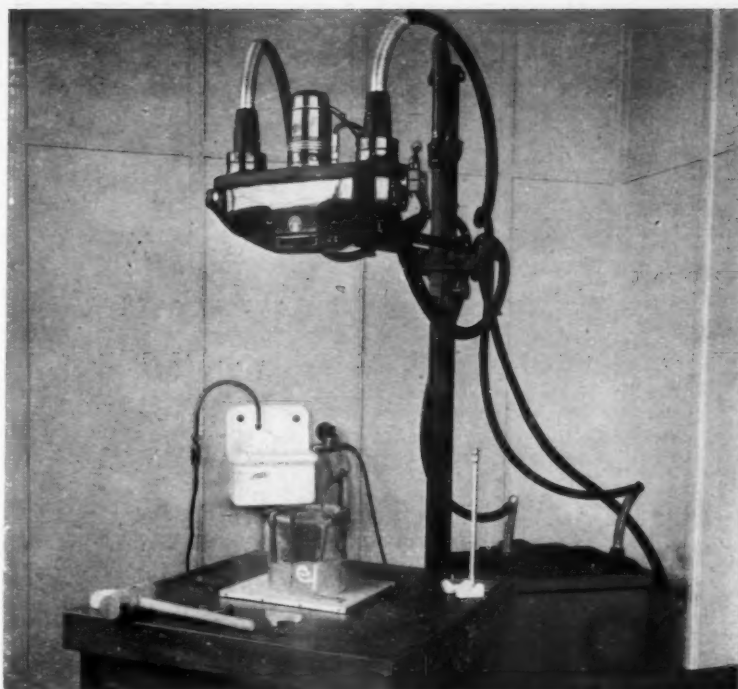
Other essential equipment in the shop are the furnaces for pre-heating the blanks. This equipment consists of Wild-Barfield batch type furnaces with a fixed hearth of heat-resisting steel to resist abrasion of sliding in and out the blanks. These are rated at 30 kw., and one is shown in Fig. 6. However, for long runs the continuous G.E.C. furnace is employed which has a heating chamber 20 ft. long by 3 ft. 6 in. wide by 9 in. deep. This furnace is split into three temperature zones each with its own thermostatic control and switch gear, whilst a Micromax temperature indicator for each zone is mounted on the control panel.

Fig. 11.—Victor KX-140 X-ray unit in the radiological department.

In connection with the general temperature control, a Kent automatic recorder is used ; this is designed to record the temperature of all three zones in such a manner that the temperature in each zone can be readily identified. To accommodate the time needed to heat blanks of varying sizes, the speed of the conveyer is adjustable through a P.I.V. gear-box that gives a stepless change over the whole range of the conveyer speeds. Fig. 7 gives a good idea of this up-to-date type of equipment.

Needless to say, the preparation of the punches and die heads are of extreme importance, and to serve the presses a very well-equipped tool shop has been installed in the main shop. The plant includes a Keller die-sinking machine.

Laboratory Control

Having produced the dies, but before any production is commenced, laboratory control steps in and tests are made of every individual extruded bar that is received before any material is released for cutting into blanks. These tests include tensile, reduction in area, percentage of elongation and examination of transverse and longitudinal sections to ensure that the physical structure is correct. An extremely well-equipped physical laboratory is provided, as will be seen from Fig. 8. Furthermore, throughout the whole process of manufacture, every piston carries a symbol identifying it with the extruded bar from which it was made. Having checked the material and before the new set of tools is released for production, sample pressings are made, inspected for dimensional accuracy and sectioned to check grain flow and grain size. Only when all this is right are the tools released. After the extruded bar has

been released it is passed to the cutting-off section, where the blanks are sawn off to pre-determined lengths established in relation to the pressing that has to be produced. Owing to the very close limits to which pistons can be pressed by this process it has been found an advantage if the blanks are weighed to a tolerance of plus or minus a quarter of an ounce, which gives some indication of the accuracy associated with the hydropress method of manufacturing pistons.

To obtain the desired physical properties in the material, after pressing it is necessary to subject these to heat-treatment. For this purpose Wild-Barfield 120 kw. furnaces are used. The usual treatment is to soak at 510° C. for 6 hours, with the temperature held to within plus or minus 5° in order to bring the hardening constituents of the alloy into solution, after which they are quenched in boiling water, where they are allowed to remain 4 hours to precipitate the hardening constituents. Vertically forced-air-circulation type furnaces are used. The temperature control equipment comprises potentiometric controllers and recorders with appropriate thermocouples. These controllers operate through a system of relays and contactor switches. Isolation and protective devices and additional contactors for the fan motor are used on the switch-gear panel. Interlocking circuits are employed so that the heating elements are only switched on when the fan is running. Elements and fan are both cut out automatically when the door of the furnace is opened. To act as an excessive temperature cut-out, in addition to the usual controllers, the millivoltmeter type indicating controller is mounted on the control panel. The control index is set a few degrees above the temperature at which the treatment is to be carried out, and in the event of the

Courtesy of Automobile Engineer.

Fig. 12.—The arrangement of the radiological dark-room, the equipment of which includes a Kodak thermostatically controlled processing unit.

ments that give much greater speed of determination with the necessary precise standard of accuracy. Included amongst the special apparatus that has been installed is a Spekker absorptiometer, for the determination of silicon and other contents, whilst to give a still greater degree of control over the production a complete X-ray equipment, shown in Fig. 11, has been installed, which is primarily used in helping to maintain the general standard of production, but is also of considerable use for development work. As the unit is intended to be used as an adjunct to production, it is essential that radiological examination is carried out quickly, and to enable this to be effective, a most modern and up-to-date dark room has been installed, with developing and fixing tanks water-jacketted and thermostatically controlled. The general arrangement of the dark room is shown in Fig. 12. A complete examination can be carried out in little more than 20 mins., and this time factor is therefore perfectly satisfactory for the use of X-ray examination on a production basis.

Completing the plant put down for the production of pressed pistons are the sand-blast cabinets and etching plant housed separately with air extractor fans. It will be appreciated, therefore, that full advantage has been taken of the latest metallurgical knowledge and of recently developed processes, to ensure the production of pistons of the highest possible quality with the maximum of consistency.

automatic temperature control failing, the excess temperature cut-out comes into operation and cuts off the current supplied to the furnace element. Not only is the furnace thus safeguarded, but also the charge itself, because the cut-out can be set to operate at a temperature lower than that at which the charge would be irreparably spoiled.

The quench tanks are of special design, being 6 ft. in diameter and 8 ft. in effective depth, electrically heated by immersion heaters fitted with thermostatic control. In addition to which, a 10 in. diameter thermograph records the temperature. Special charge carriers are used, designed to fit in place of the conventional work baskets. This keeps each layer of pistons separate, and has been adopted because, in the past, it was found that with a furnace of this size, where the weight of the charge is relatively heavy, there is the danger that the lower components may suffer deformation, It must be remembered that pistons undergoing this solution treatment are at a temperature near to softening point, and any great weight, due to the upper layer of the charge, might well cause distortion and damage to the pistons in the lower layers. Fig. 9 shows this equipment.

In equipping the chemical laboratory, shown in Fig. 10, advantage has been taken of recent develop-

Trade Publications

The advantages of using tapered roller bearings in rolling mills, especially on roll necks, is emphasised in a booklet published by British Timken, Ltd. It gives evidence, from reliable sources, indicating how the introduction of these bearings have facilitated production. The illustrations are of a very high order. Copies may be obtained from British Timken, Ltd., Cheston Road, Aston, Birmingham, 7.

Enfield Rolling Mills, Ltd., Brimsdown, Essex, have issued a folder giving useful information about a high-speed machining copper which was developed in the early days of the war and has since proved of great value in application. This copper machines as fast as free-cutting brass, using the same tools, and its properties compare very favourably with those of ordinary H.C. copper. It is regarded as a new material for the engineer.

*A*T a recent microchemical meeting, reported in our last issue, the general scientific public had an opportunity, the more conspicuous perhaps by its rarity, of seeing for itself the effect of teaching general microchemistry to otherwise ordinary students. The impression gained must have been wholly favourable, and must have prompted, in addition to admiration, the query as to why such teaching is not more widespread. The answer is in part that the system is against such a development. In order to make it worth-while to teach micro—or semi-micro—methods to a class studying for an external examination, it must be feasible to use the methods in the examination. While extensive special equipment is not necessary, certain facilities not usually available at the orthodox examination are essential. Looking from the other end, the authorities running the examinations may well plead that until there is sufficient demand for such apparatus, it is superfluous to anticipate the need. And so we have one of the all too common vicious circles. X and Y will not teach the subject until it is recognised by B, and B will not recognise it till it is taught by X and Y Such a situation is not altogether the fault of either end of the diameter of the circle. But both ends should have some sort of common meeting-place round about the centre, which, if suitably used, might go far towards eliminating the vice, and making the circle—if we may stretch the analogy so far—one of the useful wheels of industry.

The Systematic Detection of Metals on the Small Scale

By Christina C. Miller, D.Sc., Ph.D.

An account is given of the application of small scale methods to the systematic qualitative analysis of inorganic substances. Emphasis is laid on the employment of modern sensitive and selective reagents, especially organic substances, for the identification of metals.

IN the examination of inorganic materials for metallic radicals it has long been customary to apply in succession certain reagents that separate them into groups, the components of which are then further systematically isolated and identified. Early this century Emich[1] showed that the classical procedure for the common metals can be transposed to the micro scale (1–10 mg. of material), if small equipment is used and precipitates are separated from solutions by centrifuging. Benedetti-Pichler and his co-workers[2] similarly applied Noyes and Bray's[3] precise system of analysis for the majority of the metals to 1 mg. samples. Recently Benedetti-Pichler and Cefola[4] have demonstrated that it is even feasible to conduct simple analyses on the sub-micro scale ($0 \cdot 1$–$1\mu g$ of material), but mechanical and optical aids are essential and most operations need continuous microscopic observation. A third scale of operations, the semi-micro, in which 10–100 mg. of a sample may be used, will be referred to later.

When the scale of operations in qualitative analysis is reduced the importance of adequately confirming the metals present in small precipitates is increased. Before Emich's publication appeared, Behrens[5] had worked out for inorganic radicals tests that depended on the microscopic observation of characteristic crystals. These were used by Schoorl[6] for confirming all the common metals in systematic analyses on the micro scale, and later by Benedetti-Pichler and his associates,[2,4] who found, however, that the tests might fail on the sub-micro scale for lack of material to form distinctive crystals.

In addition to crystal tests Emich employed a few others based on the observation of colour, fluorescence, or luminescence. Many who lack the skilled technique of the microscopist, and hesitate to adopt small-scale methods, are attracted by the simplicity of colorimetric tests. Within the last 20 years this interest has been stimulated by the discovery of a great reservoir of colour reactions for metals. In 1905 Tschugaeff[7] had produced by the interaction of dimethylglyoxime and nickel ions an unionised compound that is bulky, intensely coloured, stable, insoluble in water, and soluble in organic solvents. These properties are characteristic

1 Emich. "Lehrbuch der Mikrochemie 1911.
2 *Mikrochem.*, 1935–38; *Ind. Eng. Chem.*, Anal. Ed., 1937–39.
3 Noyes and Bray. "A System of Qualitative Analysis for the Rare Elements," 1927.
4 *Ind. Eng. Chem.*, Anal. Ed., 1937, **9**, 483; 1942, **14**, 813; 1943, **15**, 227.

5 Behrens. "A Manual of Microchemical Analysis," 1894.
6 *Zeit. anal. Chem.*, 1907–1909.
7 *Ber. dtsch. chem. Ges.*, 1905, **38**, 2520.

of many organometallic complex compounds since discovered. Further, the reactive grouping of atoms in the organic reagent molecule may favour reaction with a particular metal, or with a limited number of metals only, in which case the reagent is *specific* or *selective* in its action. An account of these compounds has been given recently by Belcher and Spooner.[8] As tests made with organic reagents are usually very sensitive they are effective substitutes for crystal tests in micro-analysis.

Success with these unique reagents has intensified the search for sensitive and selective reagents among other organic and also inorganic substances. Many new tests are associated with adsorption phenomena, catalytic effects, induced reactions, and redox reactions. The scope and limitations of a wide variety of tests applicable to drops of solutions, and known as "drop reactions" and "spot tests," are described in the well-known book of Feigl.[9]

It is evident that if sensitive and specific reagents, that permit individual metals to be detected in the presence of large excesses of others, be eventually found for the majority of the metals, it will be un-necessary in systematic analysis to isolate the components of a mixture for identification. Instead it will suffice to apply a succession of direct tests to portions, if not of the original substance, then of groups into which the metals are first of all divided. The theme is not a new one. Half a century ago Behrens,[5] in the systematic analysis of small quantities of material, mainly on microscope slides, separated the metals into small groups and tested portions for their components by crystal tests. His methods were practicable only when similar amounts of the various metals were present. From the work of Schoorl,[6] who carefully examined the influence of an excess (100–1000 fold) of foreign elements on crystal tests for specific metals, and that of Whitmore and Schneider,[10] who applied microscopic analysis to small amounts of mixtures and alloys, it is evident that comparatively few opportunities do present themselves for the direct identification by crystal tests of several admixture metal ions.

Will the new tests accomplish what crystal tests have failed to do ? Early schemes proposed for the systematic detection of metals, in which the preliminary separation into groups was omitted, and drop reactions were applied to portions of complex mixtures, proved to be unreliable. It is now, however, fairly common practice, after separating the metals into the customary groups, to reduce the number of subsequent separations to a minimum by applying direct tests for metals to separate portions of mixtures containing a small number of mutually non-interfering metal ions. This simplification has not yet been carried very far, as several schemes[11] of semi-micro-analysis referring to the common metals show. The most usual combinations of metals dealt with are antimony and tin ; copper and cadmium ; iron cobalt, nickel, manganese, and perhaps chromium ; aluminium and zinc ; sodium, potassium, and magnesium. Weak points in most schemes are that the tests are directed essentially towards the *detection* of

metals without reference to their quantity, and that inadequate details are given regarding the limitations of the tests *under the prevailing experimental conditions*. Thus the smallest amount of metal detectable is not stated, nor is the permissible excess of other metals. Finally, the exclusion of the more prominent of the so-called uncommon metals is undesirable. Nieuwenburg and Dulfer's[12] scheme of analysis, which makes some allowance for their detection, is of very limited application.

Benedetti-Pichler and his co-workers,[2] in their systematic examination of 1 mg. samples for common and uncommon metals, retained the essential feature of Noyes and Bray's scheme but did not advocate the more direct methods of testing referred to above. Thus the components of groups of metals were successively isolated, estimated, and confirmed under conditions that permitted the detection of 5–10μg of any one in association with 500μg of the others. Comparatively few of the newer organic reagents were used either for separating metals or for identifying them. Practically all estimations were based on the bulk of a precipitate which, in the case of about 50% of the metals, was transformed into another substance for final confirmation. More than 50% of the confirmatory tests were crystal tests, and less than 20% referred to coloured solutions.

Miller (in part with A. J. Lowe)[13] has since endeavoured to simplify the chemical procedure for the detection and estimation of the metals in Noyes and Bray's groupings by making fuller use of the newer reagents. Experiments were done by semi-micro methods, the simple technique of which makes them the most popular of small-scale methods. The total weight of metals taken did not exceed 50 mg. The minimum amount of any metal ion was 250μg and the maximum, 50 mg. of a common, and 10 mg. of an uncommon metal. In seven groups about 30 metals have now been dealt with. Nearly 70% of the confirmatory tests refer to the production of precipitates of which more than two-thirds have an organic content. The remaining tests refer to coloured solutions of which 50% are produced by organic substances. Practically all estimations of quantity are based on these reactions. Whenever possible, mixtures of metals were tested for their components by applying a series of tests to small portions. Although practically every test might require, initially, special preparation of the solution, e.g., evaporation, adjustment of pH, masking of interfering substances, extraction by an organic solvent of unwanted metal ions or of the desired metal ion, etc., there was no great expenditure of time because the scale of operations was usually micro. Some encouraging results have been obtained. For example, in the combined copper and tellurium groups, after the removal of the tellurium, six metals were identified and estimated by testing separate portions of a solution containing copper, bismuth, lead, cadmium, rhenium, molybdenum, rhodium, and iridium. In the aluminium group separate tests were made for five metals in a solution containing beryllium, vanadium, tungsten, chromium, zinc, aluminium, and uranium. In four other groups there was considerable departure from Noyes and Bray's methods of analysis, but less testing for one metal in the presence of others. The analyses of many mixtures containing very variable

8 METALLURGIA, 1944, 29, 329.
9 Feigl. "Qualitative Analysis by Spot Tests," 2nd edn., 1939.
10 *Ind. Eng. Chem.*, Anal. Ed., 1930, 2, 173 ; *Mikrochem.*, 1930, 8, 293.
11 Heller and Krumholz. *Mikrochem.*, 1929, 7, 213 ; Winkley, Yanowski and Hynes. *Mikrochem.*, 1936, 21, 102. ; Engelder, Dunkelberger and Schiller. "Semi-Micro Qualitative Analysis," 1936. ; Dobbins and Southern. *Ind. Eng. Chem.*, Anal. Ed., 1942, 14, 479.

12 Nieuwenburg and Dulfer. "A Short Manual of Systematic Qualitative Analysis by Means of Modern Drop Reactions," 2nd edn., 1935.
13 *J. Chem. Soc.*, 1940, 1258, 1263 ; 1941, 72, 786 ; 1943, 72.

proportions of metals showed that the methods were reliable within the limits set.

In work of this nature substantial progress is mainly a consequence of critical investigation into the chemical principles underlying the application of new reagents. Much remains to be done but the outlook for the ultimate simplification of qualitative micro-analytical methods is not unpromising.

A brief outline of the semi-micro technique as applied to the systematic detection of metals follows.

The Experimental Technique of Qualitative Semi-micro-analysis

Reagents.—Solutions, according to their nature, are stored in 2 oz. corked bottles fitted with dropping pipettes made from 6 mm. diameter glass tubing, or in glass-stoppered bottles. Solids are kept in vials and portions removed by means of micro-spatulas made from 1–2 mm. diameter nickel wire.
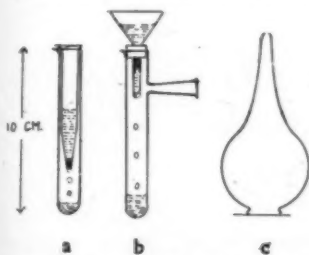

Fig. 1.—Barber's semi-micro apparatus.

Fig. 2.—Adapter for centrifuge tube.

Standard Solutions.—Solutions containing 1, 0·1, and often 0·01% of each metal ion under consideration are required for preparing standard tests in estimations of quantity, and are measured out with graduated pipettes.

Separation of Precipitates from Solutions.—It is not feasible to collect precipitates on filter papers. Barber[14] collects them on small pads of glass or cotton wool placed either in the constricted end of a tapered tube provided with a small orifice, or in the upper part of the stem of a small funnel. The former is inserted in a
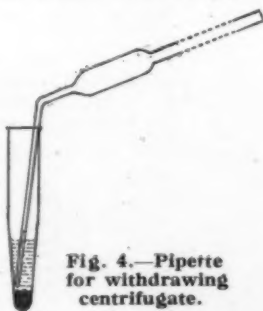

Fig. 3.— Micro-filter.

Fig. 4.—Pipette for withdrawing centrifugate.

test tube (Fig. 1a) and the latter in a filter tube (Fig. 1b). In Fig. 1a pressure is applied to the solution in the inner tube by means of a rubber ear syringe (Fig. 1c). In Fig. 1b the solution in the funnel is filtered with the aid of suction applied by depressing the rubber bulb and inserting the narrow end in the side arm of the filter tube.

In my opinion centrifugal methods of separation are more generally useful. A hand centrifuge is usually provided with two heads, one for 15 ml., the other for 1 ml. conical centrifuge tubes. For 3 ml. tubes an adapter (Fig. 2) that fits into a 15 ml. holder, can be made by soldering a short collar of brass, on which the rim of the centrifuge tube will rest, to a bent strip of the metal. An electrically-driven machine, such as the excellent International Clinical Centrifuge,[15] which is unfortunately not at present obtainable, saves time and labour. Two interchangeable heads take all sizes of conical centrifuge tubes from 0·5 to 15 ml. and also test tubes, thereby covering all normal requirements.

Fig. 5.—Capillary pipette.

A micro-filter (Fig. 3) is occasionally useful. A short 1–2 mm. capillary is drawn from 6 mm. diameter glass tubing and cut so as to leave a slightly fluted end into which a ½ in. roll of filter paper is fitted. The capillary is held vertically in the mixture and the liquid collected above the paper by mouth suction.

The Use of Centrifuge Tubes.—The tubes are seldom heated directly in flames because of their tendency to crack and of their contents to bump, and are instead inserted in a beaker of boiling water. Evaporations are expeditiously performed by allowing a current of air supplied through a capillary tube to play on the surface of the solution. Solutions that must be boiled are best transferred to test tubes or little beakers.

Group precipitates are usually formed in centrifuge tubes. Liquid reagents are added from dropping pipettes, gases delivered through fine capillary tubes, and the contents of the tubes thoroughly stirred with thin glass rods. After a precipitate has been centrifuged down, the solution can be removed by means of a bent pipette (Fig. 4). A capillary stem of 1–2 mm. diameter is carefully lowered into the liquid until the tip is within 2 mm. of the precipitate. The solution is slowly withdrawn by mouth suction, and the pipette sealed with the tip of the tongue prior to its removal. For withdrawing small volumes from 1 ml. tubes, which are held horizontally, a straight capillary pipette is gradually pushed into the liquid, which drains off by capillary action (Fig. 5). The bent pipette is excellent for separating two liquid layers from each other.

Narrow centrifuge cones need careful cleaning. Surface films are loosened with a feather and the cones repeatedly filled with water and emptied by suction (Fig. 6).

Fig. 6.—Washing of centrifuge tubes by suction.

Confirmatory Tests and Estimations of Quantity.—Precipitates are usually compared for bulk in centrifuge cones, and occasionally on small watch glasses. Precipitates and solutions are examined for intensity of colour in tubes, small crucibles or basins, or on spotting tiles. Many tests may be made on drop reaction paper, commonly by adding a drop of the test solution to a reagent-impregnated paper. Reproducibility is frequently poor, and estimations are unreliable, because
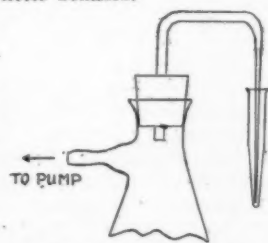
14 *Ind. Eng. Chem.*, Anal. Ed., 1940, **12**, 58.

15 Gallenkamp. "Catalogue of Laboratory Apparatus and Equipment," 11th edn., 1939, p. 785.

solutions spread irregularly. An improvement is effected by adding the solutions slowly through capillary tubes. Clarke and Hermance[16] designed a capillary burette assembly for this purpose (cf. Fig. 7). The reagent paper

Fig. 7.—Capillary burette.

is placed on a small table provided with a central opening and is brought into contact with the tip of the burette containing the test solution. By a suitable mechanism the burette is inclined at such an angle that the rate of flow is less than the rate of the reaction. Yagoda[17] confined reactions to a definite area by imbedding in the

16 *Ind. Eng. Chem.*, Anal. Ed., 1937, **9**, 292.
17 *Ind. Eng. Chem.*, Anal. Ed., 1937, **9**, 79; *Mikrochem.*, 1938, **24**, 117.

paper rings of water-repellent material (Fig. 8). The part within the ring is impregnated with an excess of the reagent and then a drop of the test solution is added. When precipitation is complete the surplus liquid is

Fig. 8.—Confined spot test paper.

drained away by placing underneath the area of reaction a mat of absorbent paper. Excellent estimations can be made.

This short outline will make it clear that an elaborate outfit is not essential and that the experimental technique is extremely simple. Comparatively few tests need microscopic observation, but a microscope is a desirable part of the equipment.

Qualitative Micro-Analysis of the Alkaline Earth Group

By R. Belcher and F. Burton

SEVERAL methods are available for the qualitative analysis of the alkaline earth group. Separation of barium as chromate followed by one of the various methods available for separating strontium and calcium (such as the ammonium sulphate or potassium ferrocyanide method) is probably the most widely used procedure. A minor disadvantage of this method is the coloration of the filtrate by chromate ion which tends to obscure later precipitates.

Another method—due to Hinds[*]—is based on the varying solubilities of the sulphites in dilute hydrochloric acid, acetic acid and water. It does not appear to have received much attention, possibly because of the readiness of these compounds to oxidise to the corresponding sulphates. A further scheme involves extraction of the nitrates with ethanol to remove calcium, conversion of the residual nitrates to chlorides by evaporation with hydrochloric acid (or heating with ammonium chloride) and the subsequent removal of the strontium chloride by a further ethanol extraction. This method is rarely used on the macro scale, because the necessary evaporations to dryness are time-consuming and because of the expense entailed by the use of ethanol, although it has the advantage that each metal is almost entirely separated.

On the micro scale the time of evaporation can be reduced considerably and the cost of the ethanol is negligible. The method has been applied on the micro scale, using the "spoon" technique described in a previous communication.[†] Separation by this method on a slide is rendered difficult by the rapid evaporation of the ethanol, whilst evaporations in the cone take

* Hinds. *Chem. Zentr.*, 1911, 1, 1556.
† Belcher. METALLURGIA, 1944.

considerably longer than in the "spoon." The scheme used is shown in the following table :—

Separation of the Alkaline Earth Group

Precipitate as carbonates in a cone following the conventional procedure, centrifuge, remove the supernatant liquid with a capillary and wash the precipitate. Dissolve in dilute nitric acid, transfer to a "spoon," and evaporate to dryness over a tiny flame, taking care not to decompose the nitrates. Extract the residue twice with ethanol—removing the solution with a finely tipped capillary—and transfer it to another "spoon."

Solution.	*Residue.*
Evaporate the ethanol. A white residue indicates Ca. To confirm, dissolve in a drop of water, saturate with solid NH_4Cl, add two drops of freshly prepared $K_4Fe(CN)_6$. White precipitate confirms Ca.	Evaporate to dryness twice, using one drop concentrated HCl each time. Extract twice with ethanol as before and transfer solution to another "spoon."
	Solution.	*Residue.*
	Evaporate to dryness. A white residue indicates Sr. Confirm by dissolving in one drop of water and spotting on paper previously treated with freshly prepared sodium rhodizonate. A red colour removed by one drop of 0·1 NHCl confirms Sr.	Indicates Ba. Confirm by dissolving in one drop of water and applying the sodium rhodizonate test. A scarlet colour not removed by 0·1NHCl confirms Ba. *Or* Dissolve residue in dilute acetic acid, add one drop K_2CrO_4 solution. Yellow precipitate confirms Ba.

NOTES.

1. If any solid particles are removed by the capillary, the tip is sealed, the capillary centrifuged, and the solution removed as in the conventional procedure. This should not occur if the solution is pipetted carefully.

2. If desired, the sodium rhodizonate tests can be applied on the spotting tile.

Hardenability of Cast Steel

NUMEROUS papers have appeared in the technical press on the subject of hardenability and the use of the end-quench test for wrought steels, and hardenability data are available for practically every type of wrought steel produced. In the introduction to a series of articles* on the hardenability of cast steel, C. W. Briggs points out that, although such investigations have been made by the steel casting industry, the papers dealt with are the first to be published regarding end-quench studies on cast steels. These investigations were carried out to show engineers and users of steel parts that the steel casting industry is actively engaged in hardenability considerations.

The hardenability range of a number of fine grained cast steels (A.S.T.M. grain size 6 to 8) were investigated by J. B. Caine. The steels included three carbon steels, containing approximately 0·2, 0·3 and 0·4% of carbon respectively, two chromium-molybdenum steels containing 0·8 to 1·0 chromium, 0·15 to 0·35% molybdenum and 0·30 and 0·40% of carbon respectively, three nickel case-hardening steels and one manganese steel containing 0·4% carbon, 1·3 to 1·6% manganese. The average hardenabilities of some comparable wrought steels are also given as a determination of a relation between the hardenability of cast and wrought steels. The wrought manganese steel contained 1·6 to 1·9% manganese.

A significant difference is found to exist between the average hardenability of cast steel and that of wrought steel. As shown by hardenability curves, all the cast steels tested with the exception of the manganese steel, have a higher average hardenability than do wrought steels of the same specified composition, and this is considered to be due to the slightly higher silicon and aluminium contents of the cast steels. In the one exception, the manganese content of the cast steel is lower than that of the wrought

steel. The theoretical hardenability of cast steel calculated from the analyses and grain size checks almost exactly with the hardenability determined experimentally in the same manner as wrought steel.

by a slight modification in analysis. The combined multiplying factor resulting from the higher silicon and from the metallic aluminium, which is added partly as a deoxidiser and partly to control grain size, in fine grain cast steel as compared with fine grain wrought steel, is about 1·2. This is partially offset by the slightly smaller

TABLE I.

COOLING RATES AND END-QUENCH DISTANCE FOR MANGANESE-MOLYBDENUM CAST STEEL MACHINED ROUNDS.

	1-in. Round		2-in. Round		3-in. Round		4-in. Round	
	Water Quench	Oil Quench	Water Quench	Oil Quench	Water Quench	Oil Quench	Water Quench	Oil Quench
Surface.								
Cooling Rate°	850° F.	120° F.	550° F.	58° F.	400° F.	39° F.	140° F.	15° F.
Distance from Quenched End†	10·5	2·5	1·0	5·0	1·25	8·0	2·5	12·5
¾ of Radius.								
Cooling Rate	220° F.	68° F.	78° F.	31° F.	57° F.	16° F.	24° F.	8° F.
Distance from Quenched End	1·5	4·0	4·0	8·0	5·0	12·0	9·5	18·0
½ of Radius.								
Cooling Rate	135° F.	55° F.	46° F.	24° F.	27° F.	12° F.	14° F.	6·5° F.
Distance from Quenched End	2·5	5·0	6·0	9·5	8·5	14·5	13·0	21·0
¼ of Radius								
Cooling Rate	115° F.	48° F.	36° F.	19° F	18° F.	10° F.	10° F.	5·5F.
Distance from Quenched End	3·0	5·5	7·0	11·0	11·0	16·0	16·0	24·0
Centre.								
Cooling Rate	100° F	45° F	32° F.	18° F.	15° F.	9° F.	8° F.	5·5°F.
Distance from Quenched End	3·0	6·0	8·0	11·0	12·5	17·0	18·0	24·0

° Cooling Rate—° F. per sec. at 1300° F.
† Distance from Quenched End in sixteenths of an inch.

As Quenched 855°C
Tempered 480°C
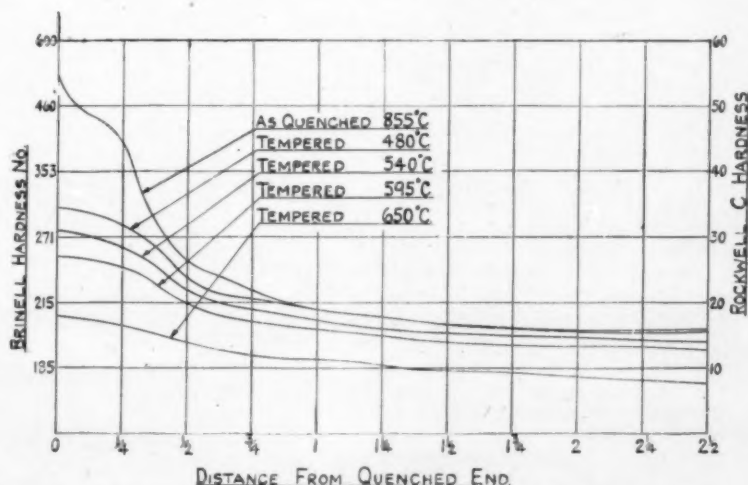Tempered 540°C
Tempered 595°C
Tempered 650°C

Fig. 1.—End quenched hardenability of a manganese-molybdenum cast steel.

In general, there is no difference in the hardenability of a steel because it is cast. The only difference between a cast and a wrought steel is produced

grain size of cast steel, but the increase in overall hardenability depends upon the type and amount of other alloys present, and the greater the
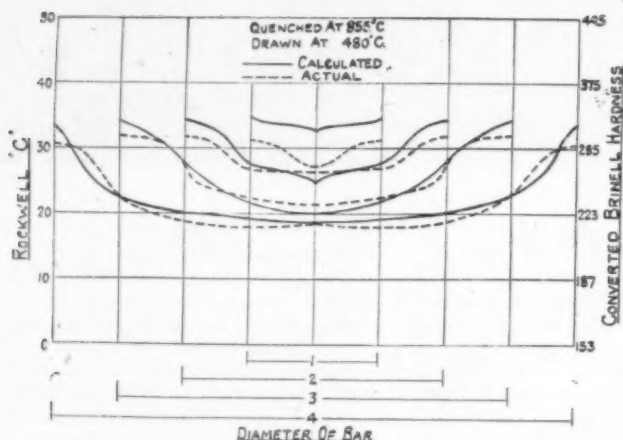
Fig. 2.—Comparison of actual and calculated hardness gradients on various sizes of quench and tempered manganese-molybdenum cast steel.

Fig. 2.—Influence of manganese. (Forbes, Paulson and Minert).

overall hardenability, the greater the effect of the silicon and aluminium. In practice, the slight difference in hardenability can be compensated by having the carbon content of cast steel not more than 0·05%.

The use of the end-quench test for cast steel is dealt with by E. J. Wellauer, who shows that one important application is that of calculating the hardness gradient across various sized rounds. The end-quench hardenability of a manganese-molybdenum cast steel was determined on bars machined to 1-, 2-, 3-, and 4-in. diameter Several end-quench bars were treated and the hardness determined after quenching at 860° C., and after quenching at tempering at 480°, 540°, 595° and 650° C. The results obtained together with the composition of the steel are given in Fig. 1. Cooling rates and end-quench distances for the various diameters are given in Table I. Using the data obtained from these tests the transverse hardness gradient can be calculated on various section sizes, Fig. 2.

The use of this method of calculation enables comparisons to be made of different heats and analyses of varying hardenabilities for definite applications, thereby eliminating the costly and laborious method of actual quenching, tempering, cross-sectioning and hardness reading. Besides determining the suitability of a given heat for a particular purpose, the method allows studies to be made to determine the variations which can be expected between the minimum and maximum ranges of hardenability and the effect of a predetermined temperature.

The various tests show that the results of the calculated and actual hardness at or near the surface compare very closely. In the centre and intermediate points a difference of 5 Rockwell C is noted and this error is about the average that is to be found when calculating the as-quenched hardness distribution across diameters up to 4 in. for both forged and cast steels, although in many instances differences of 2 Rockwell C. or less are obtained.

Hardenability data on a series of cast-steels are given by F. Kiper, standard Jominy end-tests being used from regular production heats. A cast steel containing 0·32% carbon, 1·15% manganese when compared with a wrought steel of somewhat similar composition showed slightly better hardenability properties. Tests on two typical cast steels of the manganese-molybdenum type containing 1·04% manganese, 0·4% molybdenum and 1·0% manganese, 0·24% molybdenum respectively showed the first steel to have a somewhat similar hardenability curve to the 0·32% carbon steel with which it is used interchangeable. The hardenability properties of the second manganese-molybdenum steel were somewhat lower than those obtained from the first manganese-molybdenum steel. Much better hardenability properties were obtained for a cast steel containing 1·4 to 1·5% manganese, 0·50 to 0·55% molybdenum and 0·12 to 0·15% vanadium, a hardness of 38 Rockwell C. being maintained at 2 in. from the quenched end. The curve for this steel also showed only a slight
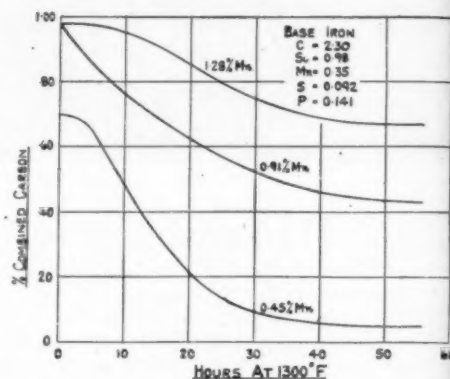
falling-off when compared with the curves of the other steels tested.

Reviewing the data in the three papers, Briggs concludes that : (1) Cast steel and wrought steel of the same composition have similar hardenabilities as illustrated by the end-quench tests. (2) Commercial cast steel will in general show slightly higher values than commercial wrought steel of the same carbon content, due to the higher silicon, aluminium, and sometimes manganese contents of cast steel, since all cast steels are dead-killed steels. (3) Hardenability of cast steel is dependent upon composition and grain size in exactly the same manner as wrought steel, (4) Data available on wrought steels can be used for cast steels of similar composition by the application of a multiplying factor. (5) End-quench tests on cast steel can be used for calculating the hardness gradients of cast steel sections in the quenched and tempered conditions. (6) The substitution of one cast steel for another to obtain similar hardenability is possible with cast steels as with wrought steels. (7) An understanding of the properties developed in castings of varying sections can be obtained by the use of the end-quench test as a routine control in steel foundry operations.

ERRATUM

In the digest of the work by C. H. Lorig, " Speeding Graphitisation of Malleable Iron," on pages 339 and 340 of our October issue, the graph shown in Fig. 2 should be replaced by the graph shown at the top of this column. A copy of this illustration will be sent on request to the editor.

Please replace the illustration on page 340 of the October issue with that given below.
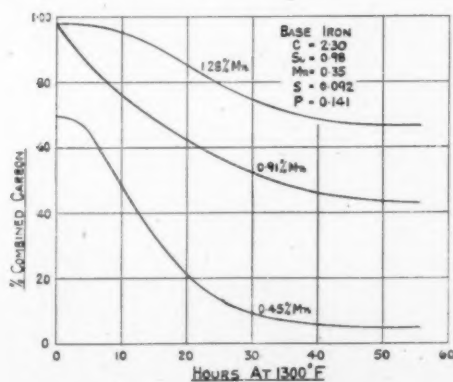

Fig. 2.—Influence of manganese.
(Forbes, Paulson and Minert).

Coreless Induction Furnaces in the Steel Foundry

By F. Harms

THE last fifteen years have witnessed a steadily increasing employment of coreless induction furnaces. While originally furnace capacity did not exceed some 110 lb. per heat, furnaces with capacities as large as 8 tons were installed during the last few years. On the whole, however, furnace capacities to-day range from 1 to 5 tons according to the purpose for which they are intended.

furnace circuit (Fig. 1) contains 46 condensers of 204 kVA. rating at 3,000 volts and 600 cycles. The ½ ton furnace is equipped with a condenser battery of 13 units with a rating of 204 kVA. at 2,000 volts and 600 cycles. The condensers are of the oil-cooled type with a cut-out thermostat set at 65°C.

The design of the furnaces is outlined in Fig. 2. The water-cooled primary coil of the 2·5 ton furnace is composed

Fig. 1.—Circuit diagram of coreless induction furnace.

The coreless induction furnace installation referred to below is employed in a foundry engaged in the production of steel castings. A first 2·5 ton furnace was installed in the Autumn of 1937. This was followed in the spring of 1938 by the installation of another unit of identical size and of a smaller furnace of ½ ton capacity. These furnaces are in continuous day and night operation, the monthly output of each 2·5 ton furnace being some 400–500 tons. The service life of the acid lining is some 140–160 heats with a new fritting being effected every 22 heats. This is considered an excellent record in view of the fact that many very hot melts of high manganese content for thin-walled castings are produced.

For local reasons the motor generators are placed at some 350 ft. distance from the working platform from whence they are remotely controlled. The generators have a capacity of 700 kw. at 600 cycles. Each 2·5 ton

with 1% boric acid added for fritting. As the furnace is acid lined, no refining is attempted. At the same time the acid lining results in very small loss of alloying constituents, vanadium losses being only 8–10%, chromium losses being some 3%, and tungsten losses being 2·5%. This type of furnace, therefore, is eminently suitable for the production of high-alloyed castings. If properly operated, manganese losses can also be kept quite low. In the production of 1·2–1·5 Mn steel, the ferro-manganese consumption amounts to 22 lb. (pure) manganese per ton of steel produced, as compared to a consumption of 27·5 to 28·6 lb. in the basic arc furnace. A few typical analyses of alloy steel castings produced with these furnaces are listed in the subjoined Table I, where the strength data given refer to the castings in annealed condition. Similar data for carbon cast steels are given in Table II.

An outstanding advantage of the coreless induction furnace is that it affords very close temperature control.
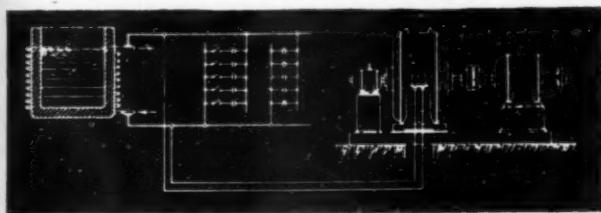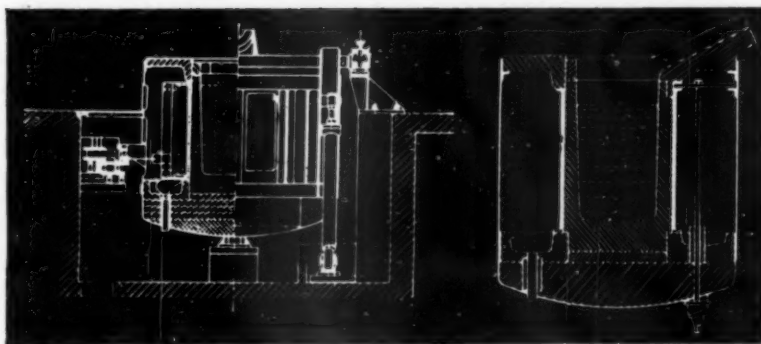

Fig. 2.—Sectional views of coreless induction furnace.

of 32 turns, its diameter being 920 mm. and its height being 940 mm. The steel shell of the furnace is shielded by means of a cylindrical copper shield, the coil being held concentrically within the latter by means of wooden filler pieces. A hydraulic device is provided for tilting the furnace 115° for pouring. The acid lining is made of ganister

This is of particular importance where very hot melts for the casting of thin-walled and of small pieces are essential. In the plant referred to, melting times range from 2 hours 30 mins. to 2 hours 40 mins., but from other installations it is known that with larger electric input, melting times of less than 2 hours can be achieved.

TABLE I.

	C	Si	Mn	P	S	Cr	Mo	V	Y.P. t/sq. in.	U.T.S. t/sq. in.	Elongation %	Reduction of area, %	Impact strength ft. lb.	Impact strength at −45° C. ft. lb.
Cr-Mo-V	0·24	0·45	1·02	0·022	0·018	1·48	0·22	0·04	78·4	82·6	10·8	47·0	31·1	18·9
Cr-V	0·29	0·44	0·72	0·02	0·014	0·93	—	0·12	61·8	65·85	15·0	56·0	70·1	34·7
Mn-V	0·3	0·42	1·35	0·017	0·019	—	—	0·17	55·8	61·1	14·8	56·0	65·8	—
Cr-Mo-V	0·4	0·47	0·63	0·025	0·013	2·29	0·25	0·11	42·7	54·1	19·0	49·0	84·6	—
Mn-V	0·29	0·47	1·18	0·027	0·016	—	—	0·11	48·3	54·5	16·5	60·0	—	—

Since in the acid furnace neither phosphorus nor sulphur are eliminated from the charge, only relatively clean scrap can be used. But actual experiences in the plant referred to have shown that an over-cautious attitude in this respect by no means is called for. Even the use of heavily rust covered material remained without influence upon the physical properties of the product. The fact that there is no carbon pick-up in the induction furnace is of considerable importance in the production of high alloy castings with low carbon content. A disadvantage of the coreless induction furnace is, however, its high capital cost which is roughly twice that of an electric arc furnace of equal capacity. With regard to specific energy consumption, both the induction furnace and the arc furnace consume 600 to 700 kwh. per ton of steel produced, but with regard to specific output the induction furnace excels by a wide margin. Also, the electric load of the latter is far more uniform than that of the arc furnace.

during the upset process and preventing an even distribution of the semi-fluid metal. Cavities are then formed during the subsequent cooling (contraction of fluid metals).

The difficulty can generally be overcome by increasing the upset force of the welding machine. This is, however, not very economical and further experiments on controlling the shape and size of the crystal grains in this zone are in hand.

The phenomenon is obviously a complicated function of the nature of the steel and the heat distribution along the weld.

It is interesting to note that for the particular kinds of steels employed in these tests, this fault zone occurred only very rarely.

The Quality of Resistance Flash Welds of High Tensile Steels

By F. Bollenrath and A. Cornelius.

THE experiments were carried out mainly with two chromium-vanadium alloy steels, one of which contained also molybdenum. The % compositions are given below :—

(2) Tempering to 870° C. for one hour followed by air cooling.

The tests covered the usual mechanical qualities such as tensile, notch

	C	Si	Mn	P	S	Cr	Mo	V
Steel A ..	0·27	0·25	0·68	0·018	0·01	2·46	0·21	0·19
Steel B ..	0·20	0·25	0·74	0·018	0·01	2·38	—	0·27

The material was available in plates 12, 20 and 25 mm. thick and 120 mm. wide, the flash buttwelds being carried out on a A.E.G. resistance welding machine employing a specific upset pressure of $\sim$ 5 Kg./$_{mm^2}$ over a travel of 4–7 mm. The material burned away corresponded to about 12–16 mm., the total welding time 30 seconds. After welding, the joint is cooled in air and subsequently heat-treated, three different processes being employed.

I. (1) Normalising at 870° C. for one hour followed by air cooling.
   (2) Reheating to 870° C. for one hour followed by oil quenching.
   (3) Tempering to 450°, 550° or 650° C. for one hour followed by oil quenching.

II. (1) Normalising at 870° C. for one hour followed by air cooling.
   (2) Reheating to 870° C. for one hour followed by oil quenching.
   (3) Tempering to 550° C. for one hour followed by air cooling.

III. (1) Heating to 870° C. for one hour followed by oil quenching.

impact, fatigue (alternating about a mean tensile of 10 Kg./$_{mm^2}$) and bending.

The principal conclusion drawn by the authors is that for the particular steels examined, the tensile strength of the weld is at least as good as that of the parent material ($\sim$ 150 Kg./$_{mm^2}$). The fatigue limit of the weld (10^7 reversals) is however appreciably lower, 10 ± 26 Kg./$_{mm^2}$ against 10 ± 32 Kg./$_{mm^2}$ for the parent material. (The fatigue results showed a considerable scatter and the figures quoted refer to the lowest values reached in each case).

The notch impact strength is roughly halved (2 m Kg./$_{mm^2}$ against an optimum value of 4 m. Kg./$_{mm^2}$ of the unwelded material. These results are moreover very little affected by the type of heat-treatment employed so that the simplified method III can be adopted and the normalising period as well as the final oil quenching omitted.

These results apply only if the welding process is carried out properly and the setting of the machine should be frequently checked and a rigorous method of weld inspection adopted.

One source of weakness is the formation of small holes and cracks in a so-called fault zone at some distance from the weld proper. This zone apparently arises from the crystal grains locking

Double Pick-up Features

New Magnetic Separator

FOR the past two years a new type of magnetic separator has been in service in the concentrator of the Richard Ore Co. at Wharton, New Jersey. The Richard Company is mining and milling iron ore. The machine, known as the Memco-Hoster wet-type magnetic separator, is a new development in the wet concentration of magnetic iron ores. It differs from the customary wet-type separator in that it has two complete separate banks of magnets, and utilises the double pick-up. Ore to be separated, which has been mixed with approximately three parts of water is fed into the machine and passes down an inclined tray. It passes under the first bank of magnets and all magnetic material is lifted up to the conveyer belt and carried across the tailing-discharge hopper, where it is delivered on to the second tray. Together with all dirty water, the tailings are immediately discharged from the machine, thus preventing contamination of the concentrates by this dirty water.

The magnetic portion which has been carried across the tailings-discharge hopper is dropped into a feed box, which is part of the second tray. At this point it is re-mixed with water and flows down the second tray. From this tray the high-grade concentrate is lifted to and carried along the second bank of magnets, being thoroughly washed by sprays and finally discharged at the end of the machine.

The second bank is divided into sections. The magnetic intensity of each section is controlled by rheostats which regulate the current input of each section, so that any grade of concentrate can be obtained by regulating the intensity of these magnets. Material passing down the second tray which has not been lifted to the magnets, together with any material washed out of the magnetic portion, discharges into the middlings hopper and is returned to the circuit for further treatment. The machine makes three products: a tailings, a true middling, and a high-grade concen-

trate. Machines are built with magnets 1 to 4 ft. (0·30 to 1·20 m.) wide. Capacity on minus-10-mesh magnetic ore containing 35 to 40% iron and producing a concentrate of 68 to 69% iron is approximately 10 tons per foot (0·30 m.) of belt-width per hour, so that a machine 4 ft. (1·20 m.) wide will handle about 40 tons per hour. The new separator is simple in operation, requires no adjustments, uses a minimum of water, needs no baffles, dams, overflow weirs, nor discharge valves or spigots. No attention is necessary to maintain water levels. The machine is fed by gravity.

Heat-Resisting Alloys for High-Temperature Stressing

By C. T. Evans

DEVELOPMENTS in the gas turbine are intimately connected with improvements in heat-resisting alloys. Such alloys must be capable of withstanding continuous high-tensile loads at high temperatures with minimum creep. At the same time they must be corrosion-resistant and withstand rapid temperature and stress variations without undergoing changes in structure or cracking. Some idea of the possibilities of heat-resisting alloys is furnished by the ultimate stress/time relationship at constant temperature. The maximum time is usually 2,000 hours and changes in ductility and impact strength under these conditions can be measured in the ruptured specimen. When plotted on a log-log scale, the ultimate stress/time relationship should produce a straight line. A change in slope indicates some structural or surface instability of the alloy at this particular temperature and load and the detection of such changes is a most useful feature of this test.

Creep tests give a record of strain against time at constant stress and temperature. Such curves usually show three well marked stages: a fairly rapid initial rise of strain with time followed by a prolonged period during which the strain increases at a very much slower rate. This is eventually followed by a second rise, leading soon after to the rupture of the specimen. Creep tests are usually

limited to relatively low stresses so that the first two characteristic stages of the curves are covered in 2,000 hours. A useful modification of the creep test is obtained by lowering the applied stress as soon as the strain reaches a definite amount. A series of "secondary" creep rates are thus obtained, the constant stress during each gradually decreasing. During the relatively short period over which these secondary creep measurements extend, the creep rate is approximately constant and plotting these rates against the corresponding stress on a log-log scale generally produces a straight line of constant slope. From this an expression for the stress remaining in a bolt made of the material and initially pulled up at room temperature can be obtained after exposure to a given temperature for a definite time.

If sufficient creep tests with different stresses at constant temperatures are available they can be replotted to give the variation of stress with time of application with strain as parameter. The resultant curves are characterised by different rates of creep and it is useful to insert amongst them a stress-time curve for which the creep exceeds the secondary stage by 10%, thus indicating that the third or dangerous stage is imminent. The curve thus corresponds to the yield point at ordinary temperatures.

Tests such as the above combined with oxidation, scaling, fatigue, and damping tests will be very useful in comparing different materials under

high temperature conditions. Since creep depends upon time, the required ultimate life of the structure plays an important part and a material which may be satisfactory in aircraft under war-time conditions with a maximum life of 1,000 hours may prove unsuitable for peace time engineering products requiring reliability over several hundred thousand hours.

Moreover, standard tests of the nature described above and carried out on wire or bar samples only form a reliable standard of comparison if the material is homogeneous and of the same quality as the finished article. The most successful heat-resisting alloys will not respond to heat-treatment in the ordinary sense and hence the manner in which they are worked and the shape of the section will have a profound effect on the resultant qualities. In many cases castings will have to be adopted since the necessary hot-working becomes too difficult. It is problematical how far test specimens cut out of such materials are representative and therefore the laboratory tests must always be supplemented by actual performance tests under practical conditions.

In spite of the tremendous impetus of the war, no outstanding development can be recorded in the field of high-strength heat-resisting alloys subjected to dynamic load.

The most promising alloys are still of the same type as those known before the war. Such progress as has been made relates rather to determining their limitations more accurately and fixing optimum load and temperature conditions in each case. None of the alloys combines the ideal characteristics at all temperatures and superiority of one over the others is generally limited to quite a narrow temperature range, the order of merit depending moreover markedly on the required stress range.

Chips for Magnesium Powder Fabrication

MAGNESIUM powder, important for flares, incendiaries, etc., is chemically pure magnesium, 99·98% or more. Its fabrication into powder of the correct fineness is fraught with many problems, a main one being to guard against fires while in process. The fabrication-process described may be termed the "hammer mill" method, to distinguish it from the ball mill

type, which is full of hazards. The raw material is received in the form of extruded rods or bars in lengths ranging from 30 in. to 12 ft. (0·75 to 3·65m.) with diameter 1·3 in. (33 mm.) The rod goes first to the chipping machine which receives rods just 28·8 in. (73 cm.) long, sawed before charging. "Chipping" consists of using cutters to chip or shred slivers from the end of the rod.

The rods are mounted into a carriage that feeds them to the cutter at a speed corresponding with the desired thickness of the chip. Five rods are mounted into the machine at a time, or about 12½ lb. (5·7 kg.) of magnesium per charge. The cutter, mounted on a mandrel, is equipped with helical cutting edges, along the edges of which saw-like points are spaced. With each

rotation of the cutter one cutting edge gouges out 14 chips per rod. Usually four such machines comprise a battery.

The chips are fine light ribbons, usually appearing singly but sometimes twined, resembling wood shavings, and are slightly over 1 in. (25 mm.) long. Usually, after a 12-hour run, the cutters have to be removed for sharpening. After several sharpenings they must be reground and teeth re-aligned. They are made of high-grade tool steel. The chipping machine is composed of but two units : the carriage or feed, and the mandrel and cutter. Chips are removed constantly by a blower and conducted to a separate building as the more segregated magnesium is, the safer. It is conducted through a copper tube to avoid static charges and sparks.

Titanium-Bearing Graphitised Pig Iron

THE problem of eliminating hard spots from grey iron castings prompted Tonawanda Iron Corporation to undertake experiments directed towards the production of a pig iron which would eliminate the effect of these impurities on the foundry casting. Titanium is a good reducing agent and has a decided effect upon the structure of the iron by decreasing the size of the graphite flakes. As a de-oxidiser it may be used to improve the fluidity of oxidised iron. Until these experiments were made, titanium had been introduced by ferro-titanium additions to the ladle. Tonawanda has perfected a blast furnace technique that permits charging titanium-bearing material in the furnace burden. A pig iron is produced in which the graphite is finely divided and evenly dispersed throughout the matrix. This graphitised condition of the pig iron persists through the melting operation in the cupola and imparts to the castings the improved properties normally associated with titanium-bearing cast iron. This pig is called G-Iron.

The method consists of charging the blast furnace with a mixture of Lake Superior hæmatite and some titanium-bearing material such as ilmenite or rutile. To reduce the titanium oxide and to completely dissolve Ti in the molten iron, the temperature in the combustion zone is maintained as high as possible and a larger than normal

From The *Iron Age*, April 27, 1944.

volume of basic slag is used. Air blast temperature is of the order of 1,500° to 1,600° F. (815° to 870° C.) and the slag volume is maintained between 1,300 and 1,500 lb./ton (650 and 750 kg./metric ton). Superheating the iron in this way not only aids in putting about 0·4 to 0·5% Ti in the iron but also in causing the free carbon to be separated out in finely divided form.

Four claims for superiority of G-Iron are made : (1) Refined and uniform grain structure, (2) greater fluidity, (3) reduction in internal shrinkage and chill, (4) better machinability. Photo-micrographs made compare the micro-structure of castings made from G-Iron and regular pig iron. In both cases 35% pig iron was used in the cupola charge and the analysis of the castings was approximately 2·1% silicon and 3·6% total carbon. In the graphitised iron casting, the combined carbon is 0·38% or six points lower than that made with regular pig iron. The casting made with regular pig iron shows segregation of graphite into pockets, a flaky structure and shrinkage cavities, while the G-Iron casting shows a uniform dispersion of the graphitic carbon and no segregation. This unusual fluidity of G-Iron as shown in a spiral fluidity test, may be accounted for by the purging of the iron from oxides and silicates which tend to produce sluggish iron.

Because of the absence of segregation and the lower combined carbon,

with the finely divided graphitic carbon uniformly distributed, improved machinability is secured despite a slight increase in the Brinell hardness. Absence of hard spots has also been achieved, with resultant increase in tool life. Both tensile and transverse strengths with G-Iron are approximately 10% above those obtained with regular pig iron.

A Statistical Survey of Failures in Aircraft Engines

By S. H. Rolle

NEARLY 6,000 cases of engine failure reported to the Aircraft Engineering Division of the C.A.A. over the period of 1/1/41 to 30/6/43 have been analysed. Of these roughly half occurred in regular transport flying and accounted for seven forced landings, involving three cases of damage to the aircraft structure, but causing no injury to passenger or crew. Engine failure during private operation on the other hand led to 2,416 forced landings, damaging 1,462 aircraft and causing 36 deaths and 187 cases of personal injuries. Nearly two-thirds of the engine failures in regular transport flying were due to the ignition system (mainly sparking plugs) whilst about one quarter were due to engine structural elements (exhaust valves, oil pressure release valves and crankshafts).

In the case of private flying, failures of structural engine elements ranked equally with carburettor troubles (40% each), whilst the ignition system only accounted for 5% of the failures.

It is interesting to note that whilst in transport flying, most of the forced landings were due to structural element failure, and none were due to ignition trouble, the majority of forced landings carried out by private aircraft were due to trouble with the fuel system.

In comparing the results of transport and private operation, difference in maintenance and size of power plant must not be forgotten. Thus only very few of the American private planes have a power output as large as 200 h.p., the great majority averaging about half this. On the other hand, almost all transport aircraft have engines exceeding 900 h.p.

Reducing Columbium Oxide and Processing Columbium

A NEW process for reducing columbium oxide to pure columbium has been announced by the Fansteel Metallurgical Corporation, North Chicago. Columbium oxide of the desired purity is prepared from columbium residues and a part of this oxide is carburised by heating an intimate mixture with lampblack in an inert atmosphere. The carbide is analysed for carbon and mixed with oxide in a ratio to give a mixture containing equal atomic proportions of oxygen and carbon. When this mixture of columbium carbide and oxide is heated in a vacuum, carbon monoxide is liberated and a columbium metal remains. The yield is only slightly less than that calculated from the equation $Cb_2O_5 + 5CbC = 7 Cb + 500$.

The metal is next converted to powder in a ball mill. Electrolytic columbium powder consists of small individual crystals. The actual Cb powder grain size may be of molecular proportions and each particle is made up of many grains. The powder is pressed into bar form at 50 tons per sq. in. (7,000 kg./cm.²). Bars intended for the production of rod or wire are made square to cross section ; those to be rolled into sheet are pressed with a width at least twice their thickness. These bars can be handled without danger of breaking and have sufficient resistance to compression to be firmly held when their ends are gripped by water-cooled terminals in the sintering furnace. The bars are heated in a vacuum by their resistance to the passage of an electric current. The furnace must be equipped with very high capacity vacuum pumps, selected and arranged so that their capacity remains high when the gas pressure becomes low. In addition to sintering the metal, this operation reduces the gas content to the lowest possible value. Oxygen especially must be removed as completely as possible since very small amounts make the metal harder and less easily annealed.

The smaller the grain size, the greater is the tendency to develop large crystals in the sintered metal. Due to the greater particle size of the powder, these bars do not shrink appreciably even when heated to the highest usable temperature. With columbium and tantalum this is an advantage since the escape of oxygen is favoured by the porosity of the metal. To compact the metal and close the pores, the bars are worked under a heavy hammer until they are reduced about 20% in thickness. They are returned to the sintering furnace and heated to weld up the new contacts formed by the mechanical working. After passing through this cycle once more, the metal is solid and free from pores. Now the bars can be hammered, swaged or rolled. Sheet can be spun or drawn into seamless tubing. All of these operations are carried out at room temperature.

Columbium is a platinum-white, soft, ductile metal. Its density, 8·4, is about one-half that of tantalum. Its linear coefficient of expansion is $7·2 \times 10^{-6}$ and the electrical resistance 17 microhm per c.c. at 68° F. (20° C.). The work function of columbium is the lowest of any of the pure refractory metals, being 3·96 volts. The literature gives 3,542° F. (1,950° C.) as the melting point. This figure is too low. The correct one is probably above 3,812° F. (2,100° C.). Columbium has been found to be as suitable as gold alloys for fountain pen nibs because it has the strength and springiness required, welds readily to iridium alloy tips, and is not corroded by acid inks. Other potential applications are in certain electronic tubes and in some chemical equipment where its lightness and toughness are advantageous.

Creep Strength, Stability of Microstructure and Oxidation Resistance of Chromium-Molybdenum and 18-8 Chromium Nickel Steels

By R. F. Miller, W. G. Benz and M. J. Day

D URING the past several years, an investigation of the effect of heat-treatment on the creep strength of various carbon-molybdenum and chromium-molybdenum steels has been in progress, the results of which have been reported from time to time. Several of the alloys which were originally tested in only one condition of heat-treatment have now been tested in an alternative condition, and some previously tested only at 540° C. have now been tested at 595° C. The investigation has been further extended to include 5% chromium-molybdenum steels, 8 to 27% chromium or chromium-molybdenum steels and 18–8 chromium–nickel steels.

The steels tested were divided into the following general groups : (A) Chromium-molybdenum steels containing 0·13 to 0·21% carbon and 0·56 to 1·95% molybdenum. (B) Chromium-molybdenum steels containing 0·08 to 0·17% carbon, 1·25 to 3·26% chromium, 0·5 to 1·06% molybdenum and 0·12 to 1·57% silicon. (C) Chromium-molybdenum steels containing approximately 5% chromium and 0·5% molybdenum with different amounts of aluminium, silicon, columbium and titanium.

(D) Chromium-molybdenum steels containing 8 to 12% chromium and 0·5 to 1·0% molybdenum and a 27% chromium steel. (E) 18–8 chromium-nickel steels with and without titanium and columbium. All the steels were heat-treated at suitable temperatures, the ferritic chromium-molybdenum steels being furnace-cooled, the austenitic 18–8 steels water-quenched and the modified 18–8 steels air-cooled. In certain cases these treatments were followed by tempering or stabilising. All specimens subjected to oxidation tests were heated at 900° C. and furnace-cooled prior to machining and testing. Creep tests were carried out on steels from groups B, C, D, and E, at 540° and 595° C. and oxidation tests were made at 595°, 760° and 925° C.

Data on creep strength—that is, the stress for a creep rate of one millionth inch per inch per hour derived from tests lasting 3,000 hours—showed that at 540° C. the creep strength of air-cooled and tempered 2·25% chromium, 1% molybdenum steel and 5% chromium, 0·5% molybdenum steel was somewhat above that of the same materials in the furnace-cooled condition. Increase of the chromium content from 2 to 9% caused little change in creep strength at 595° C. The addition of titanium or columbium to

TABLE I.
RESULTS OF OXIDATION TESTS.

Steel	Nominal Composition	Gain in Weight MG/CM² in 250 Hours at			Gain in Weight MG/CM² in 1000 Hours at		
		595° C.	760° C.	925° C.	595° C.	760° C.	925° C.
C1	5 Cr, 0·5 Mo	3·1	28·9	252	4·9	57·0	—
C2	5 Cr, 1·0 Mo	2·4	48·7	255	5·1	85·0	—
C3	5 Cr, 0·5 Mo, 1·5 Si	0·5	0·2	5·2	0·1	0·3	117
C5	5 Cr, 0·5 Mo, Ti	2·4	44·2	267	3·9	89·0	—
C6	5 Cr, 0·5 Mo, Cb	2·4	47·8	297	2·9	106·0	—
C7	5 Cr, 0·5 Mo, 1·5 Si, Ti	—	20·6	50·2	—	33·0	153
C8	5 Cr, 0·5 Mo, 1·5 Si, Cb	—	1·3	47·2	—	0·7	350
D3	9 Cr, 1·0 Mo	—	0·3	207	—	0·4	417
D4	12 Cr, 0·5 Mo	—	0·2	174	—	0·2	307
D5	27 Cr,	—	—	1·2	—	0·1	2·1
E1	18 Cr, 8 Ni	—	0·1	26·6	—	0·2	27·0
E2	18 Cr, 8 Ni, Ti	—	—	14·0	—	—	14·1*
E3	18 Cr, 8 Ni, Cb	—	—	17·7	—	—	17·7*

* 450 Hour Test.

5% chromium-molybdenum steel increased its strength at 540° and 595° C., and the addition of columbium to 8% chromium, 1% molybdenum increased its creep strength at 595° C. The creep strength of 18–8 steel at 595° C. is about the same as that of similar steel containing titanium, while 18–8 steel containing columbium has a considerably higher creep strength, all of the materials being in the water-quenched or air-cooled condition. Stabilisation of air-cooled 18–8 steel containing titanium and columbium by heating for 2 hours at 870° C. caused a decrease in creep strength.

No significant change in the hardness of the furnace-cooled chromium-molybdenum steels occurred during creep tests at 540° and 595° C., but there was a small decrease in hardness of some of the air-cooled and tempered materials. A slight increase in hardness was noted in the 18–8 steels particularly those containing columbium. The impact resistance of the chromium-molybdenum and 18–8 chromium-nickel steels decreased slightly during creep tests, except in the case of the furnace-cooled steel containing 2·25% chromium, 1% molybdenum which showed a small decrease at 540° C. A period of 3,000 hours at 510° C. produced no observable change of microstructure except in pearlitic carbon-molybdenum steels. At 540° C. a marked change occurred in carbon-molybdenum steels air-cooled, and a moderate change in similar steels air-cooled and tempered. Addition of chromium appeared to stabilise the structure of chromium-molybdenum and 18–8 chromium-nickel steels, little or no change being visible in their structures at 540° and 595° C. except in water-quenched 18–8 steel where grain boundary precipitation of carbides was apparent.

A series of 1,000-hour oxidation tests were carried out by the grain in-weight method on all the steels and the results obtained in Groups C, D and E are given in Table I. At 595° and 760° C., the amount of oxidation of the carbon-molybdenum steels was about the same as that of plain carbon steel, and there was no appreciable improvement on addition of chromium up to about 3% or of silicon up to about 0·75%. The addition of 5% of chromium was advantageous, and further increases of chromium decreased the amount of oxidation, the 27% chromium steel being the best alloy tested. Addition of 1·5% silicon markedly lessened the amount of oxidation of chromium-molybdenum steels at 595° and 760° C., the plain carbon steel, and 2 to 5% chromium-molybdenum steels oxidised completely within 1,000 hours. The 18–8 steels were somewhat inferior to the 27% chromium steel, and addition of columbium or titanium resulted in a slight decrease in the amount of oxidation at 760° C.

Wear-Resistant Castings
By R. McIntosh

TO increase the abrasion-resistance and the resultant life of parts of equipment subject to wear, nickel-chromium white iron has been successfully and extensively used in castings. The following composition limits have been found best for obtaining a material of optimum wear-resistance for the applications made :—

Total carbon	.. ..	3·40 to 3·75%
Silicon	.. ..	0·35 to 0·50%
Manganese	.. ..	0·40 to 0·70%
Nickel	.. ..	4·50 to 5·00%
Chromium	.. ..	1·50 to 1·75%

These applications, the scope of which includes one Michigan company's mining, milling and smelting operations, include: dredge-pump shell

liners, impellers, pipe and flanged elbows ; stamp shoes, mortar dies and mortar liners ; ball-mill liners ; grinding balls ; scoop feeders ; Akins spiral classifier shoes ; flotation impellers, pans and hoods ; pulleys for copper-casting wheels ; welding rod for hard-surfacing worn-down equipment.

Electro-Deposition of Copper Powder
By W. H. Osborn and S. R. Tuwiner

ATTEMPTS to produce copper powder in a standard electrolytic copper refinery are described. The investigators set out to retain the same current density, electrolyte composition and temperature which had been proved optimum for most economic refining practice. The same impure refinery anodes were to be used, allowing slimes to collect at the bottom of the tanks for intermittent removal. Electrolyte circulation was to be maintained at the rate customary in copper refineries. It was hoped that by a substitution for the oil used in preparing the brittle cathode, a deposit of copper powder might be obtained.

The method finally preferred was the application of castor oil previously oxidised with a small amount of perchloric acid to a rolled sheet anode followed by the electro deposition of copper as a powder, using the same equipment and electrolyte employed in the multiple system of copper refining.

The investigation resulted in the discovery of a crystalline metallic deposit having the following characteristics : Particles are flakes, each being a single or twined crystal, arranged in the deposit to form a cellular structure with many voids. Individual flakes are 1 micron thick. Each flake is coated with a film of oil which was applied to the cathode sheet. Copper particles grew in two dimensions only. For some reason, probably selective wetting by the oil, growth was impeded in the third dimension. The powder produced by this method is not suitable for the usual sintered metal products because of its flow characteristics and the copper particles being coated. However, this type of electrolytic flake copper powder is ideally suited to further processing either by ball milling or by stamp milling, obtaining a very fine grade of bronze powder which is especially useful in anti-fouling compositions.

Steel	Nominal Composition	Gain in Weight MG/CM² in 250 Hours at			Gain in Weight MG/CM² in 1000 Hours at		
		595° C.	760° C.	925° C.	595° C.	760° C.	925° C.
C1	5 Cr, 0·5 Mo	3·1	28·9	282	4·9	57·0	—
C2	5 Cr, 1·0 Mo	2·4	48·7	255	3·1	85·0	—
C3	5 Cr, 0·5 Mo, 1·5 Si	0·5	0·2	5·2	0·1	0·3	117
C5	5 Cr, 0·5 Mo, Ti	2·4	44·2	267	3·9	89·0	—
C6	5 Cr, 0·5 Mo, Cb	2·4	47·8	297	2·9	106·0	—
C7	5 Cr, 0·5 Mo, 1·5 Si, Ti	—	20·6	50·2	—	33·0	153
C8	5 Cr, 0·5 Mo, 1·5 Si, Cb	—	1·3	47·2	—	0·7	350
D3	9 Cr, 1·0 Mo	—	0·5	207	—	0·4	417
D4	12 Cr, 0·5 Mo	—	0·2	174	—	0·3	307
D5	27 Cr,	—	—	1·2	—	0·1	2·1
E1	18 Cr, 8 Ni	—	0·1	26·6	—	0·2	27·0
E2	18 Cr, 8 Ni, Ti	—	—	14·0	—	—	14·1*
E3	18 Cr, 8 Ni, Cb	—	—	17·7	—	—	17·7*

* 450 Hour Test.

5% chromium-molybdenum steel increased its strength at 540° and 595° C., and the addition of columbium to 8% chromium, 1% molybdenum increased its creep strength at 595° C. The creep strength of 18–8 steel at 595° C. is about the same as that of similar steel containing titanium, while 18–8 steel containing columbium has a considerably higher creep strength, all of the materials being in the water-quenched or air-cooled condition. Stabilisation of air-cooled 18–8 steel containing titanium and columbium by heating for 2 hours at 870° C. caused a decrease in creep strength.

No significant change in the hardness of the furnace-cooled chromium-molybdenum steels occurred during creep tests at 540° and 595° C., but there was a small decrease in hardness of some of the air-cooled and tempered materials. A slight increase in hardness was noted in the 18–8 steels particularly those containing columbium. The impact resistance of the chromium-molybdenum and 18–8 chromium-nickel steels decreased slightly during creep tests, except in the case of the furnace-cooled steel containing 2·25% chromium, 1% molybdenum which showed a small decrease at 540° C. A period of 3,000 hours at 510° C. produced no observable change of microstructure except in pearlitic carbon-molybdenum steels. At 540° C. a marked change occurred in carbon-molybdenum steels air-cooled, and a moderate change in similar steels air-cooled and tempered. Addition of chromium appeared to stabilise the structure of chromium-molybdenum and 18–8 chromium-nickel steels, little or no change being visible in their structures at 540° and 595° C. except in water-quenched 18–8 steel where grain boundary precipitation of carbides was apparent.

A series of 1,000-hour oxidation tests were carried out by the grain in-weight method on all the steels and the results obtained in Groups C, D and E are given in Table I. At 595° and 760° C., the amount of oxidation of the carbon-molybdenum steels was about the same as that of plain carbon steel, and there was no appreciable improvement on addition of chromium up to about 3% or of silicon up to about 0·75%. The addition of 5% of chromium was advantageous, and further increases of chromium decreased the amount of oxidation, the 27% chromium steel being the best alloy tested. Addition of 1·5% silicon markedly lessened the amount of oxidation of chromium-molybdenum steels at 595° and 760° C., the plain carbon steel, and 2 to 5% chromium-molybdenum steels oxidised completely within 1,000 hours. The 18–8 steels were somewhat inferior to the 27% chromium steel, and addition of columbium or titanium resulted in a slight decrease in the amount of oxidation at 760° C.

Wear-Resistant Castings

By R. McIntosh

TO increase the abrasion-resistance and the resultant life of parts of equipment subject to wear, nickel-chromium white iron has been successfully and extensively used in castings. The following composition limits have been found best for obtaining a material of optimum wear-resistance for the applications made :—

Total carbon		..	3·40 to 3·75%
Silicon	..	..	0·35 to 0·50%
Manganese	..	..	0·40 to 0·70%
Nickel	..	..	4·50 to 5·00%
Chromium	..	..	1·50 to 1·75%

These applications, the scope of which includes one Michigan company's mining, milling and smelting operations, include: dredge-pump shell

liners, impellers, pipe and flanged elbows; stamp shoes, mortar dies and mortar liners; ball-mill liners; grinding balls; scoop feeders; Akins spiral classifier shoes; flotation impellers, pans and hoods; pulleys for copper-casting wheels; welding rod for hard-surfacing worn-down equipment.

Electro-Deposition of Copper Powder

By W. H. Osborn and S. R. Tuwiner

ATTEMPTS to produce copper powder in a standard electrolytic copper refinery are described. The investigators set out to retain the same current density, electrolyte composition and temperature which had been proved optimum for most economic refining practice. The same impure refinery anodes were to be used, allowing slimes to collect at the bottom of the tanks for intermittent removal. Electrolyte circulation was to be maintained at the rate customary in copper refineries. It was hoped that by a substitution for the oil used in preparing the brittle cathode, a deposit of copper powder might be obtained.

The method finally preferred was the application of castor oil previously oxidised with a small amount of perchloric acid to a rolled sheet anode followed by the electro deposition of copper as a powder, using the same equipment and electrolyte employed in the multiple system of copper refining.

The investigation resulted in the discovery of a crystalline metallic deposit having the following characteristics: Particles are flakes, each being a single or twined crystal, arranged in the deposit to form a cellular structure with many voids. Individual flakes are 1 micron thick. Each flake is coated with a film of oil which was applied to the cathode sheet. Copper particles grew in two dimensions only. For some reason, probably selective wetting by the oil, growth was impeded in the third dimension. The powder produced by this method is not suitable for the usual sintered metal products because of its flow characteristics and the copper particles being coated. However, this type of electrolytic flake copper powder is ideally suited to further processing either by ball milling or by stamp milling, obtaining a very fine grade of bronze powder which is especially useful in anti-fouling compositions.